CHARGE CHARACTERISTICS, CATION COMPOSITION, AND EFFECTS OF ORGANIC AMENDMENTS ON HIGHLY WEATHERED SOILS AT DIFFERENT pH LEVELS

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By

Silvio Vega

Thesis committee:

Nguyen V. Hue, Chairperson
James A. Silva
Russell S. Yost
Robert M. Caldwell

We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Agronomy and Soil Science.

THESIS COMMITTEE

Chairperson

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CHAPTER 1

CONSTRAINTS AND PROBLEM IDENTIFICATION

The tropics is geographically defined as a region between 23.5 latitude north and 23.5 latitude south of the equator (Kanwar and Yongdahl, 1985). This area comprises 38% of the total 13.2 billion ha ice-free land of the world (Kanwar and Youngdahl, 1985; Fanning and Fanning, 1989). Oxisols are the only soil order truly confined to the tropics and cover approximately 1.12 billion ha of the total land mass (Eswaran et al., 1986). Ultisols are geographically more extensive than Oxisols; they can be found not only in the tropics but also in temperate regions, such as the southeastern USA and southern China (Fanning and Fanning, 1989). According to Eswaran et al. (1986) Ultisols cover approximately 0.73 billion ha of the total land area with 75 % of the Ultisols occurring in the tropics. Together, Oxisols and Ultisols constitute approximately 35 to 40 % of tropical soils.

Oxisols and Ultisols can have positive, neutral, or negative charge depending on the environment to which they are exposed. Variable charge characteristics of tropical soils were intensively studied in the 1970's (Van Raij and Peech, 1972; Parfitt, 1980). By the early 1980's several publications and two comprehensive books (Theng, 1980; Uehara and Gilman, 1981) have been published about this subject.

Work of Mattson (1931) on the isoelectric weathering, a process by which soils tend to approach the steady state, was

highly relevant to the understanding of acid formation of strongly weathered soils. In accordance with Mattson's theory, Uehara and Gillman (1981) proposed that soils attain equilibrium by shifting their natural pH toward the pH of their zero point of charge. Most studies on surface horizons of Oxisols and Ultisols have shown that their ZPC lies between pH 3 and 5 (Gillman and Bell, 1976; Gallez et al., 1975; Morais et al., 1975). These soils are acidic. Soil acidification through man-made fertilization such as the use of urea, ammonium sulfate is also well recognized (Bohn et al., 1985).

Consequences of soil acidification, whith respect to plant growth, are: H toxicity; Al toxicity; Mn toxicity; deficiency of Ca, Mg, and K; P, and Mo deficiency; poor root growth and limited water uptake (Marschner, 1991). Heavy inputs of SO2 and NO_x gases into the atmosphere have made rainfall in North America (USA and Canada) and Europe acidic (Krug, 1991). This "acid rain" process has contributed significantly to the acidity of lakes and rivers (Haines and Akielaszak, 1983) and soils (Krug, 1991).

Common remedies to correcting soil acidity and nutrient deficiencies are lime and fertilizers. These materials, however, are relatively expensive (Cregan et al., 1989) and may not be available to resource-poor subsistence farmers. Furthermore, because the buffering capacity of highly weathered soils is often high (Uehara and Gillman, 1981) large

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quantities of liming materials would be needed to increase soil pH to levels adequate for plant growth (Naidu et al., 1990).

Before the advent of modern agriculture, organic materials was the primary source of plant nutrients and soil amendments. Use of composts as organic fertilizers was practiced by early civilizations, such as the Romans, Greeks, and Jews (Martin and Gershuny, 1992). In fact, application of compost and organic manures (including human waste) to agricultural lands has been practiced by the Chinese, Japanese and Indians for thousands of years (Murthy, 1978). For many farmers, especially in developing countries, organic manures are still the cheapest and most available alternative fertilizers.

In recent years, concern about environmental pollution, global climate change, and declining energy resources has encouraged agricultural researchers to reconsider organic residues as an alternative to synthetic fertilizers. The ever-increasing quantity of sewage sludge produced worldwide, for instance 8.5 millions tons were produced in the USA in 1990 (Hasbash, 1990), has forced many municipalities throughout the world to face the problem of disposing of and/or recycling this material (Page et al., 1987). Therefore, interests in applying sludge to agricultural, forests, and disturbed lands has greatly increased.

Beneficial effects of organic amendments on physical, chemical, and biological properties of soils are well documented (Martin and Gershuny, 1992; Hue, 1993). Epstein (1975) reported improvement of soil physical properties such as water retention, hydraulic conductivity, infiltration, structure and aeration from sludge applications. Avnimelesh (1986) reported the beneficial effects of organic residues in reducing runoff and erosion. Organic amendments also play an important role in increasing the negative charge (or CEC) of soils (Tate and Theng, 1980). Increasing the negative charge of soils decreases ZPC in highly weathered soils (Uehara and Gillman, 1981).

Other benefits of organic materials applied to tropical soils are the increased availabilities of N and P (Constantinides, 1992; Hue, 1991); increased soil pH (Bessho and Bell, 1992; Vega et al., 1992; Hansen et al., 1989); as well as increased soil solution cation concentration and availability (Licudine and Hue, 1992). Micronutrient availability is also greatly enhanced by organic amendments (Mc Caslin et al., 1987).

Studies from Hawaii demonstrated the aluminum detoxifying effect of organic amendments (animal wastes, green manures and sewage sludge) on highly weathered soils (Hue and Amien, 1989; Hansen et al.,1989; Hue, 1992). Soil chemical composition indicates that Al reduction at increased pH, by organic amendments, is a major mechanism for Al detoxification. (Hue,

1992; Hansen et al., 1989). Other studies (Bessho and Bell, 1992; Kinraide, 1991; Suthipradit et el., 1990; Tam and Mc Coll, 1987; Hue et al., 1986;) have reported that complex formation, involving Al and organic acids released from the organic matter, was another major factor responsible for the Al detoxification.

The specific mechanism of Al detoxification by organic amendments is difficult to isolate in soils. This is because of the combined effects of increasing pH and the release of organic compounds (organic acids, organic phosphate and sulfate, antibiotics, hormones etc.) from soils. The majority of the cited compounds have been reported as Al detoxifiers in acid soils or solutions (Kinraide, 1991). Regardless of the mechanisms involved, these reports consistently demonstrate that organic residues has a beneficial effect on Al detoxification.

Potential adverse effects also exist. The most common concern is the addition of heavy metals (Hg, Pb, Cd, Ni etc) into agricultural lands when sewage sludge is applied. Heavy metals could enter the food chain. This health threat, however, is minimal when regulations and guidelines are followed (EPA, 1979). Anaerobic conditions may become prevalent following organic residues applications. Russell (1973), for example, reported that anaerobic conditions (less than 2% O_2) in the soil with high levels of methane, ethylene, and H_2S gases, reduced root growth. Epstein (1975) monitored

gas accumulation in soil 40 days after sludge application and showed that O_2 concentration dropped from 20% to 2% and CH_4 and CO_2 increased from approximately 4% to 30% to 40%, respectively.

Anaerobic conditions decrease soil redox potential and could reduce NO_3^- to NO_2^- or N_2. Potential localized toxicities of nitrite and ammonia to roots, resulting from the application of organic residues, have been described (Schmitt et al., 1992; Adriano et al., 1973). Recent studies (Vega et al., 1992; Hue, 1988) have shown that Mn toxicity can occur in manganiferous soil as a result of organic material applications. Although increased pH caused by organic amendments may decrease Mn concentration in soil solution by increasing soil pH (Foy, 1988), redox and complexation reactions could intensify it.

In conclusion, studies of variable charge soils, soil organic matter, and the interactions between these two factors are complex. This may be further complicated if the pH of the soil is changed. pH affects charge characteristics and cation composition and availability in Oxisols and Ultisols. The understanding of the interactions between organic manures and highly weathered soils at different pH levels is also incomplete and warrants a detailed investigation.

The first objective of my thesis is to review organo-metallic interactions in soils. The second objective is to evaluate the effect of soil pH on charge characteristics and

cation composition of an Oxisol and an Ultisol from Hawaii. The third objective is to investigate the effects of organic amendments on three highly weathered soils from Hawaii at three different (acid, neutral, and alkaline) pH levels.

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CHAPTER 2

SOIL ORGANIC MATTER: A GENERAL REVIEW

CONCEPT, CLASSIFICATION, AND ANALYTICAL CHARACTERIZATION OF SOIL ORGANIC MATTER.

Definitions of Soil Organic Matter (SOM) are conflicting in the literature (Bohn et al., 1985). In a strict sense, SOM is referred only to soil humus. Thus, it does not take into account the active components of the organic fraction, such as crop residues, leaf litter, weeds, worms, bacteria, fungi and actinomycete (Bohn et al., 1985). In a broader sense, SOM is defined as a mixture of plant and animal products in various stages of decomposition together with substances synthesized biologically, and/or chemically from the breakdown products of microorganisms (Schnitzer, 1986). The latter definition implies that SOM may include any carbonaceous materials from simple aliphatic compounds (hydrocarbons, alcohols and organic acids) to more complex molecules (pigments, proteins and humus). Operationally, scientists usually divide soil organic matter into two groups: non humic substances and humic substances.

The non humified materials or biochemical compounds are those substances released from the decay of plants, animals, and microbial tissues in their original or slightly modified form (Tan, 1986). The physical and chemical characteristics of these compounds are still recognizable (Schnitzer, 1982). They represent from 20 to 30 % of the organic matter in most

inorganic soils (Schnitzer, 1986), and include mainly carbohydrates, amino acids, proteins, lipids, hydrocarbons, polyphenols, hormones, and organic acids (Tan, 1986). Among those, carbohydrates are the most abundant and play an important role in improving soil structure (Martin and Gershuny, 1992). According to Stevenson and Fitch (1986), non humic substances in the soil solution vary over time because they have only a transitory existence. High amounts would be expected during periods of intense biological activity, such as following additions of crop residues to the soil (Chen and Stevenson, 1986). Among these, organic acids are of special interest because they dissolve minerals and complex metals (Tan, 1986; Chen and Stevenson, 1986).

Humic substances (humus) are described as a series of acidic yellow to black colored, moderately high molecular weight polyelectrolytes, that are formed from the chemical and biological degradation of plant and animal residues and synthetic reactions of microorganisms (Schnitzer, 1986; Chen and Stevenson, 1986). These compounds are stable in soils and characteristically dissimilar to any of the compounds occurring in living organisms (Chen and Stevenson, 1986). According to Schnitzer (1982), humic substances make up 75 to 80 % of the organic matter present in most inorganic soils and waters. Based on their solubility in alkali and acids, humic substances are partitioned into 3 major fractions: fulvic acids (FA), humic acids (HA), and humins. A typical

methodology for extraction and fractionation of SOM is shown in Fig. 2.1. All 3 fractions are similar in structure, but differ in their reactions (Pendias and Pendias, 1992). General properties of humic substances are as follows (Pendias and Pendias, 1992):

1. Fulvic acids (fulvate) - have a low degree of polymerization, high acidity and mobility, occur mainly in poor, acid soils of low biological activity.

2. Humic acids (humates) - have spherocolloidal polymerization, medium acidity and mobility, occur in weakly acid and neutral soils of high biological activity.

3. Humins - are products of aging of humates and fulvates, have a high degree of polymerization and low acidity, occur in all soils.

Despite efforts to elucidate the chemical formula of FA, HA, and Humins, no clear answer has been found. However, considerable progress have been made in characterizing their chemical components. Schnitzer (1982) presented a chemical composition model for FA and HA based on numerous analyses from soils with differing pedological origins. Major elements and functional groups of FA and HA in the model are presented in Table 2.1. A close examination of the data shows that: (i) the model HA contains approximately 10 % more C but 10 % less O than FA; (ii) the content of H, N, and S are approximately the same in both models; (iii) The total acidity and the carboxyl (COOH) groups are appreciably higher in FA than in

HA; (iv) Both models contain approximately the same concentration of phenolic OH and ketonic C=O, but the concentration of alcoholic OH and the ratio E4/E6 in FA is twice as much as in HA. Characterization of metallo-organic interactions in soil solution and water has also been largely improved by sophisticated instrumentation, including chemical analysis, Infrared Spectroscopy, Electron Spin Resonance, Mossbauer Spectra, Differential Thermal Analysis and X-ray diffraction.

CONTENT, SOURCES, AND RATE OF DECOMPOSITION OF SOIL ORGANIC MATTER.

The average "content" of SOM in the lithosphere has been estimated at 4.5 % with carbon as the main constituent (approximately 45 % by weight) (Lindsay, 1979). The actual content, however, varies considerably with climatic and geographic position. The organic matter content of surface horizons may range from less than 0.1 % in desert soils to close to 100% in organic soils (Schnitzer, 1982). Oxisols reportedly contain higher SOM than Aridisols (Fanning and Fanning, 1989). Some authors (Sanchez, 1976; Uehara and Gillman, 1981) have reported close similarities in the organic carbon content in tropical and temperate zones.

Three important "sources" of organic carbon in soils are soil humus, root exudates, and added substrates (Reddy et al., 1986). Components of soil humus (FA, HA, and humins) play an important role in long term reactions in soils because they

are stable materials and resistant to decomposition. Turn over time of 500 years for resistant fractions and 20 years for less resistant fractions have been estimated (McGill et al., 1981). Relative proportion of FA and HA varies considerably from soil to soil. Tan (1978a), working with an Alfisol, a Mollisol and an Ultisol, concluded that approximately the same amounts of FA were present in the Mollisol and Alfisol, with HA being dominant in the Mollisol. In the Ultisol, FA dominated. The reactivity of FA and HA with soil minerals is highly pH dependant (Tan, 1986).

Root exudates are organic compounds released to the rhizosphere by roots of higher plants (Reddy et al., 1986; Marschner, 1989). They include: a) Low- molecular-weight organic compounds (free exudates); b) high -molecular- weight gelatinous materials (mucilage); and c) sloughed-off cells and tissues (lysates) (Marschner, 1989). In contrast to lysates, free exudates and mucilage are released from healthy roots as either secretion or leakage. The amounts of organic carbon released are significantly increased when the root system is under stress such as water or nutrient deficiency, and anaerobiosis (Marschner, 1989). Root exudate consists approximately of 90 % carbohydrates and 10% amino acids (Barber and Gunn, 1974). The quantities released also depend on plant age. Haller and Stolp (1985) found that corn plants released considerably less exudate when 8 weeks than when 4 weeks old. The role of root exudates in correcting Fe

deficiency, especially in calcareous soils, has recently been intensively studied (Clark et al., 1988).

Added substrates are an important source of organic C in soils. Such substrates may occur naturally where vegetation or crop residues exist. Alexander (1977) reported that root biomass in the top 30 cm accounts for between 0.44 and 1.58 g of organic matter/m^2. Plant litter has been estimated to contribute between 1.0 to 15.3 tons of SOM ha^{-1} yr^{-1} (Willians and Gray, 1974). Other important C sources in terrestrial or aquatic ecosystems include sewage effluents, sewage sludge, industrial organics, as well as animal and green manures (Reddy et al., 1986).

The rate of decomposition of SOM depends not only on the content and source of the organic compounds in soils, but also on the biodiversity and climate of the microenvironment. The decomposition of SOM is accompanied by a loss of CO_2, the generation of new microbial tissues, and the release of mineral nutrients (i.e. N, P, K, Ca, Fe etc.). Approximately 55 to 75 % of the organic carbon of most crop residues and plant debris returned to soil is released as CO_2 over a 1-year period (Paul and Van Veen, 1978). Other authors (Martin et al., 1980; Scott et al., 1983) also reported that after 1-year incubation, approximately 60 to 90 % of the original carbon evolved as CO_2, 5 to 15 % was present in plant biomass, and the remainder in new humus. Sauerbeck and Gonzalez (1977) compared the decomposition rate of organic residues (wheat

straw and other plant residues) in small field plots in Germany and Costa Rica. They found that about 65 % of the added C was lost as CO_2 after 1 year from German soils and about 70 % from the tropical soils of Costa Rica. Decomposition rates of different organic materials as summarized by Martin and Haider (1986) is given in Table 2.2. The data indicate that some of the C substrates are rapidly decomposed within one week. After 20 weeks, over 50 % of most substrates have been evolved as CO_2. Soil humic acid, cedar wood, and peat moss, however, are highly resistant to decomposition.

SOIL ORGANIC MATTER AND CHEMICAL COMPLEXATION.

Soil organic matter can interact with clay in many ways (Mortland ,1986). Among these, complexation is most important. Complexation requires two components: an ionic species that behaves as a Lewis acid (electron acceptor), and a ligand that serves as a Lewis base (electron donor). Several metal ions can act as electron acceptors in the soil solution . Among them the transition metals (Fe, Cu, Zn, Cd, Ni, Mn), which have unpaired electrons in the d orbitals, are well recognized (Mortland, 1986). Elements of group IIA (ie. Ca, Mg), and IIIA (ie. B, Al) in the periodic table also have been cited as strong complexers (Lehman, 1963).

The ligands in a complex may be anions, polar or non-polar molecules. They may be of inorganic or organic origin. Ligands are often classified according to the number of donor

atoms they have that are able to bind to a metal ion. Ligands such as Cl^-, F^-, NH_3, H_2O, CH_3-COO^- that can bind through only one donor atom are called monodentate ligands. Others that have two or more donor atoms are called polydentate ligands. Ethylenediamine and oxalate ions with two electron donor groups are bidentates, and EDTA which has 6 electron donor groups is hexadentate. Reactions between polydentate ligands and metals are called chelation (from the Greek chele, meaning claws) (Lehman, 1963). The term complexation or coordination may be a better choice because it covers both mono and polydentate ligands in their complex formation.

A complexation reaction between a metal (M) and a ligand (L) with x number of moles, is illustrated as follows

$$M + xL = M\text{-}L_x$$

where the solubility constant of the reaction is:

$$K_s = (M\text{-}L_x) \; / \; (M)*(L)^x$$

The higher the stability constant the stronger the affinity between reactants and the more stable the complex. The stability of a complex increases with the number of rings formed by the ligands and the metal ions (Lehman, 1963).

Soil organic matter is the most important source of organic ligands in the soil solution (Stevenson and Fitch, 1986). Non-humic substances and fulvic acids are strong complexers (Schnitzer, 1986). Other potential organic complexing compounds in the soil solution include organic phosphates, phytic acids, chlorophyll and its degradation

products and porphyrins (Stevenson and Arkadani, 1972). Non humic substances with complexing characteristics are low-molecular-weight organic acids, amino acids, and polyphenols. Neutral and basic amino acids are adsorbed by most soils; thus they may play a minor role in complexing metals (Stevenson and Fitch, 1986). Polyphenols as a ligand may be more important in forest soils as they were reported to occur in leaf drip, stem flow, and forest litter (Stevenson and Fitch, 1986).

Low-molecular-weight organic acids can be broadly grouped into 3 categories: (i) volatile aliphatic acids (e.g., formic and acetic acids), (ii) non-volatile aliphatic acids (e.g., oxalic and citric acids), and (iii) aromatic acids (Stevenson, 1967). Relative abundance of organic acids in soils follows the order: volatile aliphatic acids > non-volatile aliphatic acids > aromatic acids (Wang et al., 1967). Huang and Violante (1986) recently reviewed the literature for concentrations of organic acids found in soil solutions (Table 2.3). Many acids do not exceed 10^{-5} M. For this reason, it has been assumed that organic acids have little importance in soil reactions. Other authors (Stevenson and Fitch, 1986; Mattigod et al, 1981), however, disagreed. They pointed out that concentration of micronutrients in the soil solution, for instance, rarely exceeds 10^{-6} M.

Higher amounts of organic acids are produced in the rhizosphere due to the increased activities of microorganisms,

especially bacteria (Stevenson and Fitch, 1986). Root exudates include many acids such as citric, oxalic, and tartaric acids capable of forming complexes (Rovira, 1969). Phenolic acids have also been found in root exudates (Rovira, 1969).

Fulvic acids (FA), play an important role in metal complexation reactions (Tan, 1986; Geering and Hodgson, 1969) According to Schnitzer (1969), the ability of FA to complex metals is due principally to phenolic OH and COOH groups in its structure. To a lesser extent, alcoholic OH, enolic OH, Ketonic C=O, and amino groups may also be involved in complex formation (Stevenson and Fitch, 1986). The large variety of functional groups in FA (as well as other humic substances), gives FA a stronger complexing ability than other organic acids derived from non humic substances which possess only COOH functional groups (Tan, 1986).

Complexation of FA with soil minerals has an important bearing on soil genesis (soil formation and mineral dissolution). Formations of spodic horizons, mollic epipedons, and an A horizon rich in organic matter of Andisols are attributed to mobilization and subsequent immobilization (precipitation) of the fulvic-metal complexes (Wright and Scnitzer, 1963; Tan, 1986). Complexation of important metals by FA is also very important to phytoavailability of the metals.

Several factors (pH, ionic strength, molecular weight, and functional groups) have been reported to influence the

complexing ability of FA in soils (Stevenson and Fitch, 1986). At a given pH and ionic strength, FA forms stronger coordination complexes with transition elements (e.g., Cu, Fe) than with other metals (e.g., Ca, Mg). FA binds trivalent cations in greater amounts than divalent ones (Stevenson and Fitch, 1986). Tan (1986) compared the pH effect (pH 2.5 and 7.0) on dissolution of microcline in the presence of FA: more Si was released at the lower pH.

SOIL ORGANIC MATTER AND REDOX REACTIONS.

Reduction-oxidation (redox) reaction is a process by which electrons are transferred from one compound (oxidizer) to another (reducer). The reaction is coupled: reduction can not occur without oxidation and vice versa. Redox reactions occur in soils under various conditions. In well aerated systems, electrons produced by O.M are accepted by O_2 (Bohn et al., 1985). In non aerated conditions, O_2 is quickly depleted, and free electrons may accumulate (Bohn et al., 1985). Clapp et al., (1986) reported that soils are considered anaerobic when redox potential (Eh) is below +350 mv at pH 7.0. Under anaerobic conditions other elements such as N, C, Mn, S, Cu etc. may effectively compete for electrons in the soil solution and undergo reduction.

SOM plays an important role in redox reactions because of organic carbon, which may be as high as 45 to 60 % of SOM (Lindsay, 1979; Martin and Gershuny, 1992). Organic carbon can have many oxidation states; it can undergo reduction or

oxidation depending on the soil environment. Oxidation states of several organic species are presented in Table 2.4. The highest oxidation state of C (C^{+4}) is represented by CO_2 and carbonates whereas CH_4 (methane) made up the lowest oxidation state (C^{-4}). Intermediate oxidation states include oxalate (C^{+3}), formate (C^{+2}), carbohydrate (C^{0}), acetylene (C^{-1}), methanol (C^{-2}), ethane (C^{-3}). Although they vary with sources (humus, root exudates, added substrates), carbohydrates $(CH_2O)_n$ are frequently reported as the major component of SOM. Martin and Gershuny (1992) reported that nearly 95 to 99.5 % of plant tissues is carbohydrate (including lignin and cellulose).

In the mineralization of glucose, for instance, where C^0 is oxidized to C^{+4}, 24 e^- are released (Lindsay, 1979).

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24e^- + 24\ H^+$$

The large number of electrons released into the soil environment after an application of organic residue, is normally accompanied by a decrease in the redox potential (Eh) as reported by Schimitt et al. (1992) and Ashgar and Kanehiro (1980). If the redox potential falls between +100 to +300 mv, reduction of Mn^{+4} and N^{+5} in soil solution occurs (Reddy et al., 1986). Further Eh values between -100 to +100 mv and -100 to -200 mv are indicative of the reduction zone for Fe^{+3} and S^{+6}, respectively.

EFFECT OF ORGANIC AMENDMENTS ON MICRONUTRIENT AVAILABILITY.

Micronutrient (Fe, Cu, Zn, Mn) deficiencies in crop plants are a worldwide problem, especially in neutral and alkaline soils (Vose, 1982). Micronutrient concentrations in the soil solution are very low (Mattigod et al., 1981). Therefore, the deficiencies may occur not only in neutral or alkaline conditions, but also in acid soils. For example, the extremely low solubility of the Fe oxide minerals [$Fe(OH)_3$] may not even satisfy the Fe requirement of higher plants at soil pH as low as 3.0 (Lindsay, 1979). However, Fe and Mn deficiency is rarely reported in Oxisols and Ultisols unless they are heavily limed (Katyal and Blek, 1985).

As mentioned before, SOM releases non-humic and humic substances capable of complexing micronutrients (Martin and Gershuny, 1992). Complexation of micronutrients by organic ligands often increases at higher pH (Sims, 1986). Thus, such reaction would increase micronutrient availability to plants in neutral or alkaline soils. This is also the reason why micronutrient fertilizers in the form of complexes (chelates) have been successfully used to correct micronutrient deficiency in calcareous soils (Norwell, 1972).

Parsa and Wallace (1979) reported that sewage sludge when mixed with a calcareous soil (a pot experiment), at a rate of 1.5%, significantly increased both dry matter yield and Fe uptake of sorghum. Abdou and El-Nennah (1980) studied the cumulative effect of disposing of sewage sludge on a

calcareous soil for up to 45 years. The total and water soluble Fe content in the soil increased six-fold, whereas NH_4OAc pH 2.8 extractable Fe increased ten-fold compared with the unamended soil. Availability of Mn and Zn were also increased. More recently, McCaslin et al. (1987) evaluated the effect of sewage sludge (0, 33.6, and 67.2 ton ha^{-1}) on a calcareous soil from New Mexico using sorghum as a test plant. They found a significant increase in the DTPA-extractable Fe and Zn content, and at the higher rate Fe deficiency was totally eliminated in sorghum. Blondel (1970) reported that yields of sorghum grown in a calcareous soil was almost doubled when the soil received a 20 ton ha^{-1} of farmyard manure. Dog manure containing 1850 mg Fe kg^{-1} and added at a rate of 1.5 % to a calcareous soil significantly increased dry matter yield of sorghum (Parsa and Wallace, 1979).

Among the micronutrients, Fe nutrition has received the most attention. This is mainly due to the widespread Fe deficiency in calcareous soils (Clark et al., 1988). Recently, scientists have identified two different strategies by which higher plants can increase Fe mobilization and uptake from the soil. (Romheld and Marschner, 1986a). Non graminaceous plants use strategy I whereas graminaceous plants (grasses) uses strategy II system (Romheld and Marchner, 1986b). These two mechanisms are universal for nearly all plant species (Clark et al., 1988). Complexation reactions are involved in both strategies. Strategy I plants when growing in Fe deficient

conditions, supply their Fe needs by using Fe complexed by siderophores (Romheld, 1987). Siderophores are organic molecules secreted in large amounts by microorganisms (mainly fungi and actinomycetes) under Fe deficient conditions (Romheld, 1987). Furthermore, the plants produce enzymes that reduce the complexed Fe^{+3} to Fe^{+2} in the root epidermis (Marschner, 1989).

Strategy II plants, however, react to Fe deficiency by releasing into the rhizosphere a group of organic substances called "phytosiderophores" (Romheld, 1987). The phytosiderophores have been identified by HPLC mainly as 3-hydroxymugineic acid (85%) with two other minor peaks (Kawai et al., 1987). In the literature, these compounds are frequently called mugineic acid. The strategies cited above do not guarantee that plants growing in Fe stressed conditions will not show Fe deficiency. In fact, different species and cultivars may show differences in their abilities to absorb Fe. Identification and selection of plant varieties that are more capable of resisting Fe deficiency are therefore emphasized (Marschner, 1989).

DETOXIFICATION OF ALUMINUM USING ORGANIC AMENDMENTS.

Extensive areas of the humid tropics are covered with Ultisols and Oxisols (Sanchez, 1976). These soils are acidic and may contain toxic levels of Al. Al toxicity is frequently cited as the most important factor limiting plant growth in acid soils with pH below 5.0 (Foy, 1984). Al toxicity may even

occur at pH levels as high as 5.5 in kaolinitic soils (Foy, 1984).

Liming is the usual method for increasing crop performance in these soils. Applications of lime ($CaCO_3$) will raise soil pH, decrease Al toxicity, and provide basic cations (Farina et al., 1980). The use of organic residues as an alternative to lime has shown promise.

Hebster (1935) first demonstrated the importance of SOM in reducing Al toxicity in acid soils. Schnitzer and Skinner (1963) found that soil organic matter apparently had some influence on the availability of Al since plants grew better in organic soils at a considerably lower pH than on mineral soils. Clark and Nichol (1966) suggested the formation of insoluble Al organic matter complexes.

Brogan (1967) reported a substantial reduction in soluble and exchangeable Al in acid soils of Georgia by organic material applications. Evans and Kamprath (1970), working with soils of the coastal plain of North Carolina, reported that soils high in organic matter often contained low amounts of soluble Al. Recent studies have supported the detoxifying effect of organic materials on Al-toxic soils (Barlett and Riego, 1972; Cabrera and Talibuden, 1977; Hoyt and Turner, 1975; Hue and Amien, 1989).

Total Al in the soil solution was a poor predictor of Al toxicity in plant growth in acid soils (Adams and Moore, 1983; Adams and Hathcook, 1984). This led Adams and his co-workers

to speculate that some of the Al they measured in "solution" was complexed by organic molecules. By partitioning the total Al (as measured by IACP) into monomeric Al (Al+3 + hydroxy-Al species) and complexed Al (Al-organic acid complexes), Hue et al. (1986) found that the latter accounted for 76 to 93 % of the total solution Al of two acid subsoils from Alabama.

Hue et al. (1986) also reported that the detoxifying capabilities of low-molecular weight organic acids were in this decreasing order: citric> oxalic> tartaric> malic> succinic> acetic. Recently, Suthipradit et al. (1991) failed to demonstrate the same protective effect of oxalic and malic acids in detoxifying Al in nutrient solution. They suggested that the higher concentration of Ca (500 uM), used in their experiment (instead of 250 uM used by Hue et al. (1986)) may have enhanced Ca competition for the organic ligand sites displacing more Al into the soil solution. In the same experiment, Suthipradit et al. (1990) also showed that fulvic acid completely alleviated the toxic effect of Al in soybean and cowpea. In addition to complexing soluble Al, organic manures also precipitate Al by raising soil pH (Hansen, 1989) as a result of ligand exchange between organic anions and terminal OH^- of the variable charge sites (Hue and Amien, 1989).

Ahmad and Tan (1986) compared effects of organic materials and lime on soybean growth, and found that lime alone yielded good results, but lime plus organic residue

(wheat straw) was more effective in reducing Al toxicity. In recent years, animal wastes, such as cattle and poultry manures, have been reported to reduce Al toxicity and increase rice (Oryza sativa) and Desmodium (Desmodium intortum) yields (Ragland and Boonpuckdee, 1986 ; Hue, 1992). In Hawaii, the addition of finely ground cowpea, leucaena leaves or pineapple (Ananas comosus) residue to an acid Ultisol and Andisol decreased extractable Al and increased plant yield (Lu and Hue, 1990; Hue and Amien, 1989).

MANGANESE TOXICITY AS AFFECTED BY ORGANIC AMENDMENTS.

In many acid soils, Mn toxicity is probably the second most important growth limiting factor following Al toxicity (Foy et al, 1988). Manganese toxicity generally occurs in manganiferous soils with pH values of 5.5 or less (Foy et al., 1988). However, it can also occur at higher pH values in compacted, poorly drained soils, where reducing conditions favor the production of Mn^{+2} (Lindsay, 1979). According to Reddy et al. (1986) the reduction zone for Mn^{+4} (MnO_2) lies between Eh values of 100 and 300 mv.

Although the application of organic wastes (i.e. crop residues, chicken manure, sewage sludge) may correct Mn and other micronutrient deficiencies by complexation, waste additions intensify Mn phytotoxicity (Ritchie, 1989). Reducible Mn content in the soil, and rate of organic residues applied may dictate the level of Mn availability in the soil solution. As pointed out in the previous section, soluble

organic molecules, especially low-molecular-weight organic acids, produced during microbial decomposition of the added wastes can complex Mn, and make Mn more available to plants (Clapp et al., 1986).

Seedlings of soybeans [Glycine max (L) Merr.] showed severe chlorosis, when grown on a soil treated with a low-Mn sewage sludge containing only 53 mg Mn kg^{-1} (Lutrick et al., 1982). These plants contained 725 mg Mn kg^{-1}. In the same experiment, as the sludge rate increased from 0 to 335 Mg ha^{-1}, Mn in corn (Zea mays L.) leaves also increased markedly from 100 to 458 mg kg^{-1}.

When different rates (0,20,40, and 80 g kg^{-1}) of a low-Mn sewage sludge were added to an alkaline Vertisol, an Andisol, and a manganiferous Oxisol of Hawaii, Mn phytotoxicity occurred in all sludge-amended treatments of the Oxisol and in the 80 g kg^{-1} rate of the Vertisol, but none in the Andisol (Hue, 1988). Such data suggest that sludge could not have been the direct source of Mn toxicity.

Recently, results from a study on a manganiferous Oxisol of Hawaii at three pHs and four sludge rates demonstrated that high pH reduced Mn toxicity in cowpea, while the organic amendment intensified it (Vega et al., 1992). Grove and Ellis (1980) found a significant increase in Mn concentrations in a sludge-amended Alfisol over the unamended control. These findings strongly suggest that the interaction between organic

matter and soil increases the solubility and potential toxicity of Mn.

Table 2.1 Analytical characteristics of model humic (HA) and fulvic (FA) acids (Schnitzer, 1978)

Element	HA	FA
	-------- %	---------
C	56.2	45.7
H	4.7	5.4
N	3.2	2.1
S	0.8	1.9
O	35.5	44.8
Functional group	----- cmol kg^{-1}	----
Total acidity	670	1130
COOH	360	820
Phenolic OH	310	310
Alcoholic OH	260	500
Quinonoid C=O + Ketonic C=O	290	270
CH_3O	60	80
E_4/E_6	4.8	9.6

Table 2.2 Decomposition of a variety of organic substances in Greenfield sandy loam, a fertile, sandy loam topsoil (Martin and Haider, 1986)

Substrate	Decomposition after, weeks*				
	1	4	12	20	28
Glycine	74	83	89	90	91
Glucose	73	82	89	90	90
2,4-D (side-chain) carbon	18	77	86	87	88
Arthrobacter sp. cells	60	79	85	86	87
Starch	48	69	81	84	86
Casein	58	72	84	85	85
Cellulose	27	52	77	79	84
Earthworms (Lumbricus rubellus)	59	72	80	82	84
Benzoic acid	68	78	82	83	84
Lima bean (Phaseolus lunatus L.) straw	36	57	75	78	79
Penicillium cells	56	72	76	78	79
Cysteine	54	69	75	77	78
Azotobacter chroococcum cells	61	69	74	76	78
2,4-D ring carbon	6	65	71	73	75
Azotobacter polysaccharide	3	27	61	65	68
Caffeic acid	40	60	67	68	68
Wheat straw	26	45	59	63	67
Sudangrass [Sorghum sudanese (Piper) Stapf]	34	54	64	65	66
Aspergillus glaucus cells	26	41	50	52	54
Walnut wood	7	28	45	52	53
Cow manure	18	33	43	48	50
Almond shells	12	24	37	39	41
Douglas-fir [Pseudotsuga menzieesii (Mirbel) Franco] wood	2	5	15	29	34
Ponderosa pine (Pinus ponderosa Dougl.) needles	12	23	28	30	32
Catechol	11	18	22	24	26
Peat moss	<1	3	8	14	17
Aspergillus glaucus melanin	3	6	8	9	10
Incense cedar wood	<1	<1	1	2	3
Soil humic acid	<1	<1	1	1	2

* Percentage added C evolved as CO_2. Incubation 22+/-22 °C

Table 2.3 Concentration of organic acids in soil solution (Huang and Violante, 1986).

ORGANIC ACIDS	CONCENTRATION IN SOIL SOLUTIONS (x 10^{-5} M)
Acetic	265-570
Amino	8-60
Benzoic	7.5 or less
Citric	1.4
Formic	250-453
Malic, Tartaric, malonic	100-400
Oxalic	6.2
Tannic acid related compounds (gallic acid, tannins, and other phenolic acids).	5-30

Table 2.4. The oxidation state of carbon in several organic species (Lindsay, 1979).

COMPOUND		OXIDATION STATE
$CO_2(g)$, H_2CO_3, HCO_3^-, CO_3^{-2}	(carbonate)	+4
$H_2C_2O_4$, $HC_2O_4^-$, $C_2O_4^{-2}$	(oxalate)	+3
$HCOOH(g)$, $HCOO^-$	(formate)	+2
$CO(g)$, CO	(carbon monoxide)	+2
CH_3COO, CH_3COO^-	(acetate)	0
C6H1206	(glucose)	0
C	(graphite)	-1
$CH_3CHO(g)$	(acetaldehyde)	-1
$C_2H_2(g)$	(acetylene)	-2
$C_2H_4(g)$	(ethylene)	-2
CH_3OH	(methanol)	-2
$CH_3CH_2OH(g)$	(ethanol)	-3
$CH_4(g)$	(methane)	-4

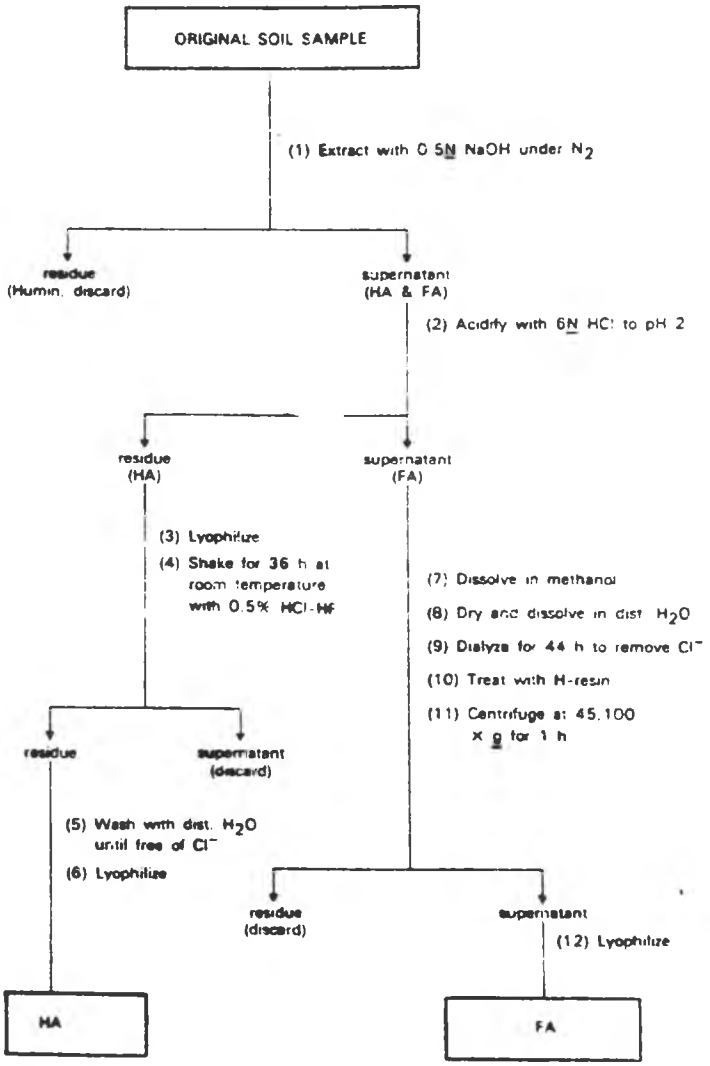

Fig 2.1 Procedures used for the extraction and purification of HA's and FA's.

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CHAPTER 3

EFFECT OF pH ON CHARGE CHARACTERISTICS AND CATION COMPOSITION OF A HIGHLY WEATHERED OXISOL AND ULTISOL FROM HAWAII.

ABSTRACT

An Oxisol and an Ultisol from Hawaii were either acidified with dilute HCl or limed with $Ca(OH)_2$ and incubated at field-capacity moisture content. Effects of soil pH on charge characteristics and concentrations of soluble cations (Al, Mn, Ca, Mg, K, Na) and DTPA-TEA pH 7.3 extractable micronutrients (Fe, Mn, Zn, Cu) were studied. Results obtained by the potentiometric titration and delta pH method indicate that the zero point of charge (ZPC) of the Oxisol and Ultisol lies at pH 3.60 and 3.65, respectively. Formation of positive and negative charges were highly pH-dependent in both soils. Relative to the Oxisol, the buffering capacity of the Ultisol increased with liming but decreased with acidification. The concentrations of soil solution cations increased considerably with acidification, but were unaffected, decreased or increased with liming. Soil solution bases (Ca, Mg, K, Na) present a highly correlated hyperbolic relationship with solution pH. DTPA-extractable Cu, Mn, and Zn generally decreased linearly with increasing pH. Extractable Fe decreased with both acidification and liming.

INTRODUCTION

Interest in variable-charge soils has increased during the last 20 years due to the intensive agricultural development in highly weathered tropical soils and to the successful application of charge development theory for amphoteric substances to such soil systems (Bowden et al., 1980). Since the classical work of Van Raij and Peech (1972), several publications (Keng and Uehara, 1974; Espinoza et al., 1975; Gallez et al., 1975; Marcano and McBride, 1989; Naidu et al.,1990) have dealt with charge development in soils under various conditions.

Variable charge in soils arises mainly from the presence of two amphoteric constituents: a) inorganic materials such as sesquioxides and, b) organic matter (Parfitt, 1980). Inorganic soil constituents with amphoteric surfaces are Al(OH) and/or Fe(OH) groups, such as gibbsite, imogolite, allophane, goethite, ferrihydrite and other sesquioxides (Bohn et al., 1985). Complexes of organic matter with iron and aluminum and the broken edges of some clay minerals such as kaolinite also possess amphoteric characteristics (Parfitt, 1980). These materials are normally found as end products of highly weathered soils such as Oxisols and Ultisols (Uehara and Gillman, 1981).

In contrast to minerals with constant surface charge (e.g., mica, montmorillonite, illite, vermiculite, chlorite etc.), where the negative charge is derived almost entirely

from isomorphous substitution, surface charge in amphoteric materials is commonly derived from the adsorption of ions onto the surfaces (Uehara and Gillman, 1981; Parfitt, 1980). The primary charging ions of the solid phase of highly weathered soils are H^+ and OH^- (Bowden et al., 1980). Other specifically adsorbed ions such as phosphate, sulphate, and silicate also have been reported as charging ions in the soil system (Bowden et al., 1980; Mekaru and Uehara, 1972).

The magnitude and sign of the soil surface charge may not only depend upon pH, but also upon the nature and concentration of electrolytes present in the soil solution (Parks, 1967). Van Raij and Peech (1972) compared the effects of different concentrations (0.01 M, 0.1 M, 1 M) of NaCl on the formation of surface charges in some Oxisols and Alfisols from Brazil. They found that considerably higher amounts of negative and positive charges were developed when the soil were treated with higher concentration of the same electrolyte. Likewise, Keng and Uehara (1974) demonstrated that the same concentration of different electrolytes (e.g. 0.1 M of NaCl, $CaCl_2$, Na_2SO_4) also may result in different surface charges in highly weathered soils.

Convenient references used for predicting amphoteric charge behavior in highly weathered soils are the zero point of charge (ZPC), zero point of titration (ZPT), point of zero net charge (PZNC), and delta pH. The ZPC is the pH at which the net surface charge from all sources is zero (Parks and de

Bruyn, 1962). The ZPT is the equilibrium pH of the soil before the addition of acids or bases (Parker et al., 1979). PZNC is the pH at which the difference between total negative charge (CEC) and the total positive charge (AEC) is zero (Marcano and McBride, 1989). Delta pH is the difference between 1M KCl and H_2O suspension pH (Uehara and Gillman, 1981).

Soil pH also markedly affects the availability of cations (Ca, Mg, K, Na, Al, Mn, Fe, Zn, Mn, Cu) in a variable charge soil (Bohn et al., 1985). In Hawaii as in many tropical regions, where highly weathered soils predominate, studies on cation composition at different pH levels are scarce and incomplete. Recently, Naidu et al (1991) and Gillman (1991) emphasized the importance of soil solution data in assessing nutrient availability for soil fertility programs. Furthermore, as Uehara and Gillman (1981) pointed out, the performance and the behavior of tropical soils (especially highly weathered soils) may be so different from their temperate counterparts that methodologies used in the quantification of cations in temperate soils may not be easily extrapolated to tropical soils.

Micronutrient measurement and diagnosis in tropical soils are problematic (Vleck, 1985). Ritchey et al. (1986) reported Zn deficiency, a serious problem, in the Cerrado region of Brazil. Recently Lindsay and Cox (1985) addressed the need for calibration of micronutrient soil tests and the lack of consistent yield response with calibration studies in the

tropics. Nevertheless, they reported that the DTPA-TEA pH 7.3 solution was most suited for assessing micronutrient availability in the tropics.

Objectives of this investigation were to evaluate the surface charge characteristics, the cation composition in the soil solution, and the DTPA-extractable cations of an Oxisol and an Ultisol from Hawaii at different pH levels.

MATERIALS AND METHODS

SOIL CHARACTERIZATION.

Two highly weathered soil from the island of Oahu, Hawaii were used in this investigation. The soils were from an Ap horizon of an Oxisol (Clayey Kaolinitic Isohyperthermic, Rhodic Eutrustox; Wahiawa series) and a Bt1 horizon of an Ultisol (Clayey Oxidic Isothermic, Rhodic kandiudult; Paaloa series). Some chemical and mineralogical data for both soils are presented in Table 3.1. Samples were air-dried, ground to pass a 6 mm sieve, then moistened to field capacity. Soil solution was collected by a centrifugation method (Adams et al., 1980). Soil solution pH was measured immediately to avoid significant CO_2 loss. Soil pH in 1M KCl and H_2O suspension were measured using a soil solution ratio of 1:1. Total Organic and soluble oxidizable carbon were determined by dichromate oxidation (Allison, 1965) and the Mn (III)-pyrophosphate method (Barlett and Ross, 1988), respectively. Effective CEC was calculated by summation of bases extracted by the neutral 1M NH_4OAc pH 7.0, and 1M KCl exchangeable acidity. Major

mineralogical compositions were analyzed by the X-ray difraction technique. All determinations were made in duplicate.

CHARGE CHARACTERISTICS.

Potentiometric titration of net surface charge. Net surface charge and the zero point of charge (ZPC or pH_o) were determined by using a slight modification of the method outlined by Van Raij and Peech (1972). These authors suggested the saturation of 4 grams of air-dry soil in 20 ml of a specific electrolyte (i.e., KCl, NaCl, $CaCl_2$) at different concentrations (i.e., 1M, 0.1M, 0.01 M, 0.001M), then the addition of acid or base to cover a desired range of pH. After equilibration, the change in pH is measured and the ZPC is determined after correction for charge development from the electrolyte used. For this paper several 1-kg sample of air-dry soil were treated with increasing rates of HCl (0 to 10 $cmol_{H+}Kg^{-1}$) or $Ca(OH)_2$ (0 to 50 $cmol_{OH}Kg^{-1}$). Acidified or limed soil samples were incubated in plastic bags at field water holding capacity for 2 weeks. Then, 20 g samples (oven-dry equivalent) were suspended in 20 mL H_20 or 1M KCl (1:1 soil-solution ratio) to measure changes in soil pH. This approach was used because the ZPC is a point at which adsorption of protons is independent of the ionic strength (Lewis-Russ, 1991; Parfitt, 1980); thus soil pH in 2 electrolytes would be sufficient to measure the ZPC and the net electric charge.

The amount of H^+ or OH^- adsorbed by the soil sample at any given pH was taken as the amount of H^+ or OH^- added to the soil minus the amount of acid or base required to bring 20 mL of deionized water and 1M KCl to the same pH. The ZPC was identified as the point (pH) where the two curves intersected or where the difference between the two pHs was zero. The net surface charge was calculated from the amount of H^+ and OH^- adsorbed with respect to the ZPC.

Total charge determination by adsorption of ions. Total negative and positive charges in the Paaloa Ultisol and Wahiawa Oxisol were determined by the method proposed by Schofield (1949) and Van Raij and Peech (1972). Duplicate 2-g soil samples (oven-dry equivalent) were weighed in preweighed centrifuge tubes and washed with 30 mL 0.1 M NaCl to minimize interferences from soluble cations. After discarding the supernatants, the residues were treated with 20 mL of 0.1 M NaCl and the pH adjusted with NaOH or HCl to give a pH range between 2.5 and 9.5. The samples were equilibrated at room temperature by shaking intermittently on a reciprocal shaker for 12 hr. Then the samples were centrifuged and the supernatant discarded. The residues were subjected to 3 additional washings with 0.01 M NaCl to ensure a complete saturation of the exchange sites with Na and Cl ions (Schofield, 1949).

After these washings the centrifuge tubes were weighed again to account for entrapped 0.01 M NaCl solution. The

residues were shaken with 20 mL 0.5 M KNO_3 for 30 minutes, then centrifuged and a 10 mL sample of the supernadant was collected. This process was repeated 4 more times to completely displace exchangeable Na and Cl ions along with the trapped NaCl solution. Then, the five 10 mL samples from each washing were combined for analysis. Na and Al in the solution were determined by Atomic Absorption spectrophotometry and the catechol violet method (Dougan and Wilson, 1974), respectively. Chloride was measured with a chloride selective electrode (Orion Research, Cambridge, MA) having a 10 % KNO_3 filling solution. The amounts of cations (Na^{+1} and Al^{+3}) and anion (Cl^-) retained after correction for the occluded salt solution, were expressed as total negative (CEC) and positive (AEC) charge, respectively (Van Raij and Peech, 1972).

Charge characterization by delta pH. The net negative or positive charge of a soil can be inferred from its delta pH (Uehara and Gillman, 1981). To obtain delta pH these authors suggested that soil pH be measured in a very dilute and a more concentrated electrolyte. In this study delta pH is defined as the difference between 1MKCl pH and H_2O pH (delta pH= pH_{KCl} - pH_{H20}). Twenty g of the treated soils were placed in 50 mL plastic beakers and mixed with 20 mL of H20 or 1M KCl. After 30 minutes, pH of the suspension were measured with a Fisher Accumet model 800 pH meter using a combination electrode. Delta pH was then plotted against pH_{H20} to reveal the ZPC and sign of the net charge.

CATION EXTRACTION AND DETERMINATION.

Soil-solution cations (Al, Mn, Ca, Mg, K, Na) were extracted by a centrifugation method (Adams et al., 1980). Micronutrients (Fe, Cu, Zn, and Mn) were extracted with a DTPA-TEA pH 7.3 solution (Lindsay and Norvell, 1978). Ca, Mg, K, Na, Fe, Cu, Mn, and Zn concentrations were determined using an Atomic Absoption Spectrophotometer. Soluble Al was determined by the catechol violet method (Dougan and Wilson, 1974).

RESULTS AND DISCUSSION

ZPC AND NET SURFACE CHARGE BY POTENTIOMETRIC TITRATION. Surface charge of the Ultisol and Oxisol as a function of pH is shown in Figs. 3.1 and 3.2, respectively. The intersection of the two curves was taken as the ZPC. The ZPC for the Ultisol lies at pH 3.65, and for the Oxisol at pH 3.60. The close and low values of the ZPC of the two soils may be related to the soils' mineralogically similar composition and high organic matter content (Table 1). Accumulation of organic matter has been identified as the main factor responsible for shifting the ZPC toward a lower pH (Gallez et al., 1976; Gillman and Bell, 1976; Van Raij and Peech, 1972). For this reason, the ZPC of surface horizons are usually lower than that of their subsoils (Morais et al., 1976).

The low ZPC of the Paaloa Ultisol (Bt1 horizon) is probably caused by the relatively high organic carbon content in lower horizons of this soil (Soil survey investigation

report No. 29, 1976). In fact, the Paaloa series was formerly classified as "tropohumult" (Soil survey investigation report No 29, 1976). High precipitation in the area where this soil naturally occurs may be responsible for the leaching of humic substances from the upper to lower horizons (Wright and Schnitzer, 1963). The low ZPC of the Paaloa Ultisol is in agreement with the result of Keng and Uehara (1974). Although the horizon of their Paaloa soil was not reported, the ZPC for that soil was 3.70.

Low values of ZPC for surface horizons of Oxisols are not uncommon. Table 3.2 lists ZPC values reported in the literature for surface horizons of Oxisols (called Ferralsol in the FAO classification system). They were between pH 3.5 to 4.5.

It is worth noting that the Zero Point of Titration (the pH of the unamended soil) did not coincide with the ZPC (Figs. 3.1 and 3.2). In both soils the ZPT was higher than the ZPC, indicating that negative charge predominated under natural condition. This has been attributed to the presence of permanent charges (Van Raij and Peech, 1972). The amount of negative charge found between the ZPT and ZPC could be measured by quantifying the amount of dilute HCl needed to lower the pH to the ZPC. This was 0.7 $cmol_{H+}Kg^{-1}$ for the Ultisol and 6.0 $cmol_{H+}Kg^{-1}$ for the Oxisol. The higher kaolinite and organic matter content as well as higher initial pH (ZPT) in the Oxisol probably accounted for this difference. Reports

on soils having ZPT higher than the ZPC is frequent in the literature (Marcano and McBride, 1989; Hendershot and Lavkulich, 1978; Gallez et al., 1976). Gillman and Bell (1976) working with Ap horizons of several highly weathered soils from Australia reported that in all cases the ZPT were higher than the ZPC. Interestingly, they found that the ZPT approached the ZPC or was even below in few cases for lower horizons.

The magnitude of the net surface charge is influenced by the pH as well as the concentration of the equilibrating electrolyte (Figs. 3.1 and 3.2). Depending on pH, three situations are possible. The first situation occurs where the ZPC equals the soil pH: the soil has no net charge ($pH_{KCl} = pH_{H20}$). In the second situation, the ZPC is higher than the soil pH: the soil surface is positively charged ($pH_{KCl} > pH_{H20}$. In the third and most common situation the ZPC is lower than the soil pH: the soil is negatively charged ($pH_{KCl} < pH_{H20}$).

Although this study made no attempt to calculate the surface charge mathematically, the non linear behavior of the curves in Figs. 3.1 and 3.2 seems to follow the model proposed by Gillman and Uehara (1980). These authors suggested the use of the Gouy-Chapman double layer equation combined with the Stern layer theory to calculate the surface charge of tropical soils. Van Raij and Peech (1972) used a similar approach to compute the surface charge of their soils and obtained good agreement between experimental and computed values.

ZPC BY DELTA pH METHOD.

Another estimate of the ZPC of the Oxisol and Ultisol was obtained from delta pH (pH_{KCl} - pH_{H2O}). The ZPC calculated from delta pH agreed well with the ZPC obtained by the potentiometric method. These were 3.60 and 3.65 for the Oxisol and Ultisol respectively (data not shown). Gillman and Bell (1976) measured the ZPC of six highly weathered soils from Australia using the potentiometric titration (NaCl as the supporting electrolyte) and the delta pH (pH_{KCL} - pH_{H2O}) method. Both methods gave the same ZPC values for three soils and a slight difference of 0.1 unit for the other three. The similarity in the ZPC obtained by both methods is apparently due to the negligible effect of the electrolytes used (1M KCl and H_2O) in developing extra charge on the soil system. In the potentiometric titration method the measurement of the blank effect on charge development is strongly recommended (Lewis-Russ, 1991). In this investigation, the effect of H_2O and 1M KCl on charge formation was virtually non-existent. According to G. Uehara (personal communication) the negligible effect from neutral unbuffered electrolytes on charge development is expected owing to their no buffering characteristics. The implication of delta pH is important in practice. If the amount of acid or base added is quantified, delta pH can yield not only information on the sign of the net charge, but also the ZPC and the net surface charge of the soil.

TOTAL CHARGE AS MEASURED BY THE ION ADSORPTION METHOD.

Both the Ultisol (Fig.3.3) and the Oxisol (Fig.3.4) possessed positive and negative charges. The positive charge (AEC) increased as pH decreased, and reached 0.90 $cmol_{+}Kg^{-1}$ in the Ultisol and 0.60 $cmol_{+}Kg^{-1}$ in the Oxisol at pH 2.5 (the lowest pH tested). The results agree well with those of Morais et al. (1976), Gallez et al. (1976), and Marcano and McBride, (1989). Above pH 5.5, positive charge approached zero which is in agreement with the result of Marcano and McBride (1989) but in contrast to that of Naidu et al. (1990). Small amounts of positive charge found at pH > 7.5 may have been derived from the isomorphous substitution of Ti(IV) and Mn(IV) by Fe(III) as hypothesized by Tessens and Zauyah (1982). Considerable amounts of titanium oxide have been found in the Paaloa Ultisol (Sherman et al., 1968), and significant amounts of Mn oxides in the Wahiawa Oxisol (Asghar and Kanehiro, 1980). Naidu et al. (1990) found a considerable amount of positive charge in highly weathered soils from Fiji at pH higher than 7.5.

Effect of soil pH on the formation of negative charge (CEC) is even more striking (Figs. 3.3 and 3.4). Negative charge ranged from approximately 0.5 $cmol_{-}Kg^{-1}$ at pH 2.5 to 10.5 $cmol_{-}Kg^{-1}$ at pH 9.5 in the Ultisol, and from 1.5 $cmol_{-}Kg^{-1}$ at pH 2.5 to 12.8 $cmol_{-}Kg^{-1}$ at pH 9.5 in the Oxisol. The small amount of negative charge at lower pHs in both soils probably resulted from soil organic matter and the isomorphous

substitution within the lattices of the constant surface charge minerals (Bolland et al., 1975; Morais et al., 1976). In fact, both soils contain approximately 10 % mica and 2.3 to 3.3 % organic carbon (Table 1). Similar results were reported by van Raij and Peech (1972). These authors found that a considerable amount of negative charge was still present at pH 2.5 in the Ap horizon of an Oxisol from Brazil. Application of lime increased soil pH and the negative charge in both soils, a result similar to that of Naidu et al. (1990).

Fig 3.3 and Fig 3.4 demonstrated the importance of soil pH to the formation of positive and negative charge in Ultisols and Oxisols. Thus, the pH at which CEC is determined must be specified. Although 1 M NH_4OAc, pH 7.0 may work well in measuring CEC of temperate soils, it may severely overestimate CEC of highly weathered soils. Gillman (1979) compared several extractants used in CEC measurement of highly weathered soils from Australia. He reported that the NH_4OAc, pH 7.0 overestimated the CEC of some soils by as much as 5 times more than the CEC measured with unbuffered (indifferent) electrolytes.

The measurement of the CEC and AEC also revealed that the approximate point of zero net charge (PZNC) for the Ultisol is at pH 2.7 (Fig 3.3). This indicates that the PZNC is 0.95 pH unit lower than the ZPC. In the case of the Oxisol, the negative charge predominated in the whole range of pH studied; therefore, the PZNC could not be measured. Similar results in

which the PZNC was lower than the ZPC have been reported by van Raij and Peech (1972), Marcano and Mc Bride (1989), and Bowden et al. (1980). These results also indicate that the potentiometric titration and the ion adsorption methods commonly used to measure surface charge characteristics of highly weathered soils do not give equivalent results. Recently, Marcano and McBride (1989) compared both methods using Oxisols from Brazil. They concluded that surface charge estimated by the two methods did not agree well, specially when the soil pH was adjusted away from the ZPC.

SOIL BUFFERING CAPACITY.

The amounts of $Ca(OH)_2$ or HCl required to change soil pH differed for the two soils (Fig. 3.5). This may be partially due to a difference in the initial pH (Naidu et al., 1990) but mainly to the buffering capacity of the soils (Uehara and Gillman, 1981). The resistance of a soil to change pH upon acid or base additions is called soil buffering capacity (Bradfield, 1923). With liming, the Ultisol seems more resistant to pH changes than the Oxisol. For instance, the amount of lime required to increase soil pH from 5.0 to 6.0 was approximately 4.0 $cmol_{OH}Kg^{-1}$ for the Oxisol and 6.0 $cmol_{OH}Kg^{-1}$ for the Ultisol. This may be due to a higher content of sesquioxides in the Ultisol (Table 1). According to Uehara and Gillman (1981) the surface hydroxyls of sesquioxides can undergo deprotonation after lime application. The protons (H^+) released react with the OH^- from lime to form H_2O, resulting in

no change in pH. This view is supported by the work of Naidu et al. (1990), who found that Fijian soils which have high buffering capacities have high levels of oxalate-extractable Fe and Al.

With acidification, however, the Oxisol showed a higher buffering capacity than the Ultisol (Fig 3.5). For instance, the quantities of H^+ needed to lower the pH from 4.4 to 3.5 were approximately 1 $cmol_+Kg^{-1}$ and 7.4 $cmol_+Kg^{-1}$ for the Ultisol and Oxisol, respectively. The higher negative charge in the Oxisol might partly account for this higher buffering capacity. More H^+ ions have been adsorbed by the negative sites on the Oxisol than on the Ultisol. These results indicate that the measurement of the buffering capacity is important not only for limed soils but also for acidified soils.

EFFECT OF pH ON CATION SOLUBILITY.

The solubility of cations (Al, Mn, Ca, Mg, K, Na) was markedly affected by pH (Tables 3.3 and 3.4). Effect of pH on soluble Al and Mn will be discussed for the acidification study whereas pH effects on soluble Ca, Mg, K, and Na will be shown for both the acidification and liming studies.

Soluble Al and Mn. Additions of dilute HCl decreased solution pH and increased soluble Al and Mn (Tables 3.3 and 3.4). Such increases can be quantified, for instance, by comparing the total soluble Al concentration in the unamended soil and in the acidified treatment (10 $cmol_{H+}Kg^{-1}$ added). Soluble Al

increased from 0.35 mgL^{-1} to 1425.17 mgL^{-1} in the Ultisol and from 0.18 mgL^{-1} to 854.81 mgL^{-1} in the Oxisol. Soil buffering capacity has a strong effect on the solubility of Al in both soils (Tables 3.3 and 3.4). In the Ultisol, for example, application of 0.4 $cmol_{H+}Kg^{-1}$ decreased soil solution pH from 4.45 (unamended sample) to 3.97 and increased total soluble Al from 0.35 to 5.95 mg L^{-1}. In the Oxisol, the application of 4 $cmol_{H+}Kg^{-1}$ decresed soil pH from 4.68 to 4.37 and increased soluble Al from 0.18 to 1.10 mg L^{-1}. The low buffering capacity of the Paaloa Ultisol could make plants grown in this soil more vulnerable to Al toxicity. Soluble Al as low as 0.5 mgL^{-1} may significantly reduce plant growth (Bohn et al., 1985).

Increased soluble Al at low pH values seems to be related to the variable charge characteristics of the soils. Decreased negative charge accompanied with increased positive charge at low pH may have released more Al into the soil solution. Furthermore, low soil pH may dissolve Al-bearing minerals such as gibbsite, kaolinite and illite (Lindsay, 1979). Dissolution reactions predict that approximately 2,700 and 27 mgL^{-1} of soluble Al can be maintained by gibbsite and kaolinite, respectively, at pH 3.0 (Zhang et al., 1991). The Paaloa Ultisol has approximately 13% of gibbsite and 20% of kaolinite whereas the Wahiawa Oxisol has 6% and 35% of gibssite and kaolinite, respectively (Table 3.1). The higher concentration of soluble Al released by the Paaloa Ultisol than the Wahiawa

Oxisol may be related to the higher gibbsite content in the Ultisol.

A close relationship (r^2=0.98) between total soluble Al and soil solution pH was found in both soils (Figs 3.6 and 3.7). Similar relationships have recently been reported for acid soils of the south Pacific islands (Naidu et al., 1991; Curtain et al., 1990). Figs. 3.6 and 3.7 also show the relationship between soil solution Mn and soluble pH. High coefficient of determination (r^2) of 0.94 and 0.89 for the Ultisol and Oxisol, respectively also indicate the pH dependency of soluble Mn. The quantities of Mn released in the Wahiawa Oxisol were significantly higher than those in the Paaloa Ultisol. For example the application of 10 $cmol_{H+}Kg^{-1}$ released 1056.20 mg Mn L^{-1} in the Oxisol but only 7.68 mg Mn L^{-1} in the Ultisol. This difference can be attributed to soil mineralogy. The Ultisol contain less than 0.1 % of total Mn (Huang et al., 1989), whereas the Oxisol has more than 2 % total Mn (Fujimoto and Sherman, 1948; Asghar and Kanehiro, 1980). The principal mineral in the Oxisol is reportedly lithiophorite (H. Ikawa, personal communication).

Soluble Ca, Mg, K, and Na. Table 3.1 shows that the unamended Oxisol (Ap horizon) contains nearly 5 times more exchangeable bases than the Ultisol (Bt1 horizon). Similarly, the unamended Oxisol has appreciably higher concentrations of soluble Ca, Mg, and K than the Ultisol (Tables 3.3 and 3.4). Based on these chemical properties the Wahiawa series has been

classified by the U.S. soil taxonomy system as an Eutrustox meaning a nutrient-rich Oxisol. Soluble Na, however, is considerably higher in the unamended Paaloa Ultisol (Table 3.3). Juang and Uehara (1968) found mica in the Paaloa Ultisol with high Na content. These authors suggested that the formation of this Na-rich mica was proportional to the quartz content in the Paaloa soil. A quartz content of 8% was found in the Paaloa soil whereas no quartz was detected by X-ray analysis in the Wahiawa soil.

Additions of dilute HCl increased soil solution Ca, Mg, K, and Na regardless of soil type (Tables 3.3 and 3.4). Increasing concentrations of soil solution cations at lower pH may be explainable by the charge characteristics of the soil. Decreasing CEC and increasing AEC (Figs 3.3 and 3.4) at low pH caused more basic cations to be released into the solution phase. In the Paaloa Ultisol, soil solution Na increased considerably with acidification; so did soil solution Ca, Mg and K. Despite the increase, soil solution K was quite low in the Paaloa Ultisol. Application of dilute HCl to the Wahiawa soil increased all soil solution cations, with soil solution Ca being the greater or highest, followed by soil solution K and Mg. Soil solution Na was low in the Oxisol.

With liming, the Ca concentration in both soils significantly increased until a pH close to 8.0 where it started to decrease. Precipitation of Ca as $CaCO_3$ at pH close to 8.0 appears to be the principal cause of this decrease

(Lindsay, 1979). Although the concentration of carbonate ions was not measured in this experiment, equilibrium relationship of carbonate species shows that bicarbonate ions (HCO_3^-) may increase considerably at increasing pH levels. Boxma (1972) working with calcareous soils from the Netherlands has reported concentrations of bicarbonate as high as 600 ppm. Increasing amounts of soluble HCO_3^- in limed soils were also reported by Curtin and Smillie (1983). The Ca concentration in the Oxisol was always higher than in the Ultisol. Application of 20 $cmol_{OH}.Kg^{-1}$, for instance, increased Ca concentration to 1150 mgL^{-1} in the Oxisol but only 217 mg L^{-1} in the Ultisol.

Liming also increased slightly soil solution Mg concentrations in both soils. Such increases, however, disappeared when lime applications exceeded 10 $cmol_{OH}.Kg^{-1}$. Furthermore, soil solution Mg decreased to about 1 mg L^{-1} in both soils when lime was added at concentration higher than 30 $cmol_{OH}.Kg^{-1}$ (Tables 3.3 and 3.4). Grove et al. (1981) and Curtin and Smillie (1983) reported that soil solution Mg concentrations decreased with liming. Recently, Carran (1991) found that Ca may induce Mg deficiency (Ca:Mg imbalance), which causes a yield decrease in clovers. Soluble Mg in the Oxisol was higher than in the Ultisol over a range of pH, but the Mg/Ca ratios in both soils were quite similar.

Liming decreased soil solution K concentration over the whole pH range in the Ultisol. In the Oxisol, however, a small increase in soil solution K was observed at the first two

increments of lime. Lowering soil solution K by liming has been reported by Barlett and McIntosh (1969) and Curtin and Smillie (1983). Soil solution K concentration in the Ultisol decreased gradually from 3.4 mg L^{-1} to 0.2 mg L^{-1} with liming (Table 3.3). Although following the same trend, soil solution K concentration was considerably higher in the Oxisol (Table 3.4). Soil solution Na also decreased in both soils with liming (Tables 3.3 and 3.4).

Finally, a regression analysis was performed on soil-solution cation concentration against soil-solution pH (Figs 3.8 to 3.15). This study uses data from both the acidification and the lime titration experiments with pH ranging from approximately 2.5 to 9.5. Although there was a poor linear correlation between all soil solution cations and solution pH, interestingly all of them showed a hyperbolic relationship when plotted against soil pH. Coefficient of determination (r^2) higher than 0.92 were found in all cases.

EFFECT OF pH ON MICRONUTRIENT AVAILABILITY.

The DTPA-TEA pH 7.3 method was developed by Lindsay and Norvell (1978) for extraction of micronutrients in calcareous and alkaline soils. Later, its use has been extended to tropical soils. Data on DTPA-extractable Cu, Fe, Mn, and Zn in soils receiving different levels of acid or lime additions are presented in Tables 3.5 and 3.6. Extractable Fe in both soils decreased with either acidification or liming. Decreased amounts of DTPA-extractable micronutrients with increasing pH

via liming have been well recognized (Lindsay, 1979). Decreasing amounts of DTPA-extractable Fe after soil acidification, however, is intriguing. Although both soils have similar amounts of Fe-bearing minerals (Table 1), considerably more Fe was extracted from the Paaloa Ultisol than from the Wahiawa Oxisol. The highest amount of Fe extracted from the Paaloa soil was approximately 550 mg Kg^{-1}, whereas in the Oxisol extractable Fe did not exceed 40 mg Kg^{-1}. Low amounts of extractable (and presumably low available) Fe from the Wahiawa Oxisol might have been caused by high amounts of total Mn in this soil, as explained by the following equation (Hem, 1964).

$$2Fe(OH)_3 + Mn^{+2} + 2\ H^+ = MnO_2 + 4\ H_2O + 2\ Fe^{+2}$$

Lindsay and Norvell (1978) suggested that a DTPA-extractable Fe concentration of 4.5 mg Kg^{-1} may be adequate for most crops in calcareous soils. The amounts of extractable Fe listed in Tables 3.5 and 3.6, which are much higher than 4.5 mg Kg^{-1}, indicate that Fe deficiencies are not expected to be a problem in both the Oxisol and the Ultisol, irrespective of soil pH. However, the Fe/Mn ratio must be considered before appropiate conclusions can be drawn in terms of Fe nutrition of plants grown in highly weathered tropical soils.

DTPA-extractable Mn decreased with increasing pH in both soils (Tables 3.5 and 3.6). Extractable Mn was considerably higher in the Oxisol than in the Ultisol. Lower pH dissolved more Mn-bearing minerals; thus, higher amounts of Mn were

extracted. Critical level of DTPA-extractable Mn for corn was reportedly 1 mg Kg^{-1} (Lindsay and Norvell, 1978). In the Ultisol, extractable Mn ranged from 6.1 to 1 mg Kg^{-1} suggesting this soil could become Mn deficient, especially at high pH. In contrast, extractable Mn levels in the Wahiawa Oxisol were all above 200 mg Kg^{-1}, indicating a potential Mn toxicity.

Extractable Zn levels were only slightly affected by soil pH (Tables 3.5 and 3.6). Nearly an order of magnitude more Zn was extracted from the Wahiawa Oxisol than the Paaloa Ultisol. Given the critical level of Zn for corn as 0.8 mg Kg^{-1} (Lindsay and Norvell, 1978) the Paaloa Ultisol is marginally Zn deficient. In fact, Zn deficiency has been documented for this soil (Rashid, 1986). Zn deficiency is a widespread problem in acid soils of the Cerrado region of Brazil (Ritchey et al., 1986). These authors found that the critical level of DTPA-extractable Zn for soybeans and corn cv.IAC-2 grown on a Cerrado Oxisol was approximately 0.7 mg Kg^{-1}.

The concentration of extractable Cu decreased with increasing pH in both the Wahiawa and Paaloa soils (Tables 3.5 and 3.6). Higher Cu levels were found in the Wahiawa Oxisol than the Paaloa Ultisol. Both soils contain more Cu than the 0.2 mg Kg^{-1} deemed critical value for plant growth (Lindsay and Norvell, 1978).

The relationship between DTPA-extractable micronutrients and suspension (1:1 soil:water) pH is presented in Fig 3.16 for the Ultisol and in Fig 3.17 for the Oxisol. These figures

reveal that DTPA-extractable Mn and Cu decrease linearly (r^2 >0.85) with increasing pH. DTPA-extractable Zn, however, shows a poor linear correlation with pH. DTPA-extractable Fe vs pH follows a parabolic pattern. Except for Fe, the concentrations of DTPA-extractable micronutrients generally decrease with increasing pH.

SUMMARY and CONCLUSIONS

The effect of pH on charge characteristics and cation solubility and extractability can be summarized as follows.

* The zero point of charge (ZPC) lies at pH 3.60 for the Oxisol and pH 3.65 for the Ultisol.
* The PZNC was below the ZPC in both soils.
* The delta pH method seems to be as effective as the potentiometric titration method in measuring the ZPC and the net electric charge.
* Buffering capacity of the Oxisol was smaller than that of the Ultisol when lime is added. With acidification, the Oxisol has a higher buffering capacity than the Ultisol.
* Soil solution Al and Mn increase exponentially with decreasing soil pH.
* Soil solution Ca, Mg, K, and Na followed a hyperbolic relationship with solution pH.
* Increasing pH decreased DTPA-extractable Mn, Cu, and Zn concentrations. Extractable Fe decreased with both acidification and liming.

* The Wahiawa Oxisol may have Mn toxicity problem whereas the Paaloa Ultisol may have Mn deficiency problem.

* Zn deficiency could be a problem in an overlimed Paaloa Ultisol.

Table 3.1 Selected chemical and mineralogical properties of the unamended soils used in the study.

SOIL PROPERTIES	SOIL	
	WAHIAWA OXISOL	PAALOA ULTISOL
1. CHEMICAL COMPOSITION		
Total Organic Carbon, %	3.25	2.30
Soluble Organic Carbon, mgL^{-1}	84.5	74.6
pH in 1M KCl (1:1)	4.05	3.85
pH in H_2O (1:1)	4.70	4.40
Soil-solution pH	4.80	4.45
KCl-extractable Al, $cmol_c Kg^{-1}$	1.20	2.05
Sum of bases, $cmol_c Kg^{-1}$	5.09	1.04
2. MINERALOGICAL COMPOSITION (%)		
Hematite	28+/-9	25+/-6
Kaolinite	35+/-9	20+/-5
Goethite	7+/-2	16+/-4
Gibbsite	6+/-2	13+/-3
Mica	11+/-3	10+/-3
Quartz	nd*	8+/-2
Magnetite	9+/-2	3+/-1
Anatase	nd	2+/-1
Amorphous materials	5+/-1	5+/-1

* non detectable

Table 3.2 pH at the Zero Point of Charge for the surface horizons of some highly weathered soils from the tropics.

SOIL GREAT GROUPS*	SOIL ORIGIN	SUPPORTING ELECTROLYTE	ZPC	REFERENCE SOURCE
Acrohumox	Sao Paulo, Brazil	NaCl	3.7	Van Raij and Peech, 1972
Acrorthox	Sao Paulo, Brazil	NaCl	4.0	Van Raij and Peech, 1972
Xanthic Ferralsol	Queensland, Australia	NaCl	3.5	Gillman and Bell, 1976
Orthic Ferralsol	Queensland, Australia	NaCl	4.0	Gillman and Bell, 1976
Haplorthox	Peninsular Malaysia	KCl	4.35	Tessens and Zauyah, 1982
Acrustox	Cerrado region, Brazil	KCl	4.34	Marcano and Mc Bride, 1989
Gibbsihumox	Hawaii, USA	NaCl	4.40	Keng and Uehara, 1974

* U.S. Soil taxonomy or FAO classification system

Table 3.3 Average soil solution composition of the Ultisol as affected by soil pH through acidification and liming.

Amendm. source	cmol H or OH Kg^{-1}	pH	EC	Al	Mn	Ca	Mg	Mg/Ca	K	Na
			dS m^{-1}	mg L^{-1}						
HCl	10.00	2.56	14.3	1425	7.68	179	82.2	0.46	35.6	131
HCl	8.00	2.63	11.3	1402	6.68	102	77.1	0.75	31.2	121
HCl	6.00	2.79	8.70	707	6.19	59.1	71.4	1.21	28.2	117
HCl	4.00	3.00	5.55	511	5.12	56.4	67.0	1.18	24.0	113
HCl	2.00	3.28	2.68	143	3.63	36.3	46.9	1.29	13.0	90.1
HCl	1.00	3.54	1.64	55.4	1.44	29.0	41.2	1.51	9.94	82.6
HCl	0.80	3.63	1.28	26.6	1.19	27.3	35.9	1.31	8.66	79.0
HCl	0.60	3.78	0.95	15.0	0.83	22.9	31.1	1.36	7.84	76.4
HCl	0.40	3.97	0.80	5.95	0.42	17.4	16.3	0.94	7.17	59.7
HCl	0.20	4.15	0.58	1.22	0.21	7.40	7.06	0.95	5.85	53.2
NONE	0.00	4.45	0.25	0.35	0.06	2.50	1.76	0.70	3.43	35.0
$Ca(OH)_2$	2.00	5.28	0.32	0.12	0.09	20.1	2.87	0.14	1.89	30.4
$Ca(OH)_2$	4.00	5.49	0.38	0.06	0.11	32.8	3.64	0.11	1.58	25.6
$Ca(OH)_2$	6.00	5.80	0.46	0.01	0.07	44.9	3.71	0.08	1.47	25.6
$Ca(OH)_2$	8.00	6.05	0.53	0.01	0.06	83.1	4.72	0.06	0.84	31.1
$Ca(OH)_2$	10.00	6.25	0.62	0.01	0.01	118	5.33	0.05	0.66	32.8
$Ca(OH)_2$	20.00	7.03	1.03	0.01	0.01	217	2.46	0.01	0.63	26.5
$Ca(OH)_2$	30.00	7.56	1.23	0.01	0.02	276	1.22	0.004	0.32	27.2
$Ca(OH)_2$	40.00	7.79	1.28	0.21	0.03	301	0.84	0.002	0.32	24.4
$Ca(OH)_2$	50.00	8.09	1.21	0.94	0.04	267	0.40	0.001	0.21	19.3

Table 3.4 Average soil solution composition of the Oxisol as affected by soil pH through acidification and liming.

Amendm. source	cmol H or OH Kg^{-1}	pH	EC dSm^{-1}	Al	Mn	Ca	Mg	Mg/Ca	K	Na
				---------- mgL^{-1} ----------						
HCl	10.00	2.98	14.5	855	1056	2280	292	0.13	702	10.8
HCl	8.00	3.09	12.2	534	895	2146	282	0.13	675	9.44
HCl	6.00	3.34	10.5	307	883	1710	259	0.15	648	7.62
HCl	4.00	3.60	7.35	112	607	1079	190	0.17	270	4.47
HCl	2.00	3.77	4.00	23.5	264	331	47.2	0.14	191	1.76
HCl	1.00	4.09	2.61	4.54	134	154	45.2	0.29	121	1.14
HCl	0.80	4.16	2.18	3.10	93.1	127	39.9	0.31	98.3	0.75
HCl	0.60	4.30	1.65	2.05	69.8	113	35.7	0.32	78.7	0.45
HCl	0.40	4.37	1.42	1.10	42.8	106	34.5	0.32	73.2	0.34
HCl	0.20	4.44	1.11	0.50	18.8	76.1	23.4	0.31	52.1	0.11
NONE	0.00	4.68	0.78	0.18	4.65	20.0	10.0	0.50	26.4	0.05
$Ca(OH)_2$	2.00	4.81	1.08	0.07	1.06	106	13.4	0.13	76.6	0.05
$Ca(OH)_2$	4.00	5.13	1.48	0.04	0.27	201	19.1	0.09	79.4	0.04
$Ca(OH)_2$	6.00	5.87	1.80	0.01	0.21	357	22.6	0.06	42.9	0.03
$Ca(OH)_2$	8.00	6.19	2.33	0.01	0.04	513	26.6	0.05	47.4	0.02
$Ca(OH)_2$	10.00	6.63	2.65	0.01	0.12	665	26.2	0.04	42.9	0.01
$Ca(OH)_2$	20.00	7.58	3.25	0.01	0.28	1150	3.30	0.003	40.8	0.01
$Ca(OH)_2$	30.00	7.82	2.68	0.01	0.08	740	1.64	0.002	13.7	0.01
$Ca(OH)_2$	40.00	8.48	2.30	0.01	0.15	580	0.41	0.0007	8.7	0.01
$Ca(OH)_2$	50.00	9.28	2.17	0.05	0.10	319	0.30	0.0009	5.7	0.01

Table 3.5 DTPA-extractable micronutrients in the Paaloa Ultisol.

cmol H^+ or OH^- added	pH	Fe	Mn	Zn	Cu	Fe/Mn
		----------mg Kg^{-1}----------				
10.00	2.80	144	6.10	1.50	3.20	24
8.00	2.90	144	5.40	1.40	3.16	27
6.00	3.00	153	4.75	1.30	2.96	32
4.00	3.20	250	4.30	1,28	2.80	58
2.00	3.45	324	4.60	1.30	2.70	70
1.00	3.50	330	3.60	1.20	2.58	92
0.80	3.60	390	3.20	1.70	2.50	122
0.60	3.70	410	2.90	1.40	2.45	141
0.40	3.80	478	2.80	1.30	2.40	171
0.20	4.05	510	2.72	1.15	2.40	187
Unamended	4.40	550	2.60	1.20	2.30	212
2.00	4.75	260	2.16	1.15	2.30	120
4.00	5.10	192	2.05	1.15	2.10	94
6.00	5.50	138	1.96	1.10	2.00	70
8.00	5.75	119	1.80	0.80	2.10	66
10.00	6.15	91.6	1.70	0.75	1.80	54
20.00	7.20	70.0	1.68	0.85	1.76	42
30.00	7.83	54.4	1.32	0.90	1.32	41
40.00	8.23	46.8	1.00	0.95	1.40	47
50.00	8.50	38.0	1.20	1.20	1.43	32

Table 3.6 DTPA-extractable micronutrients in the Wahiawa Oxisol.

H^+ or OH^- added	pH	Fe	Mn	Zn	Cu	Fe/Mn	cmol
			mg Kg^{-1}				
10.00	3.40	32.0	526	8.55	18.0	0.06	
8.00	3.50	32.4	489	7.60	17.9	0.07	
6.00	3.60	30.7	469	6.15	17.5	0.06	
4.00	3.80	30.5	459	5.60	17.7	0.07	
2.00	4.05	29.8	431	5.75	17.3	0.07	
1.00	4.30	27.6	408	5.25	17.2	0.07	
0.80	4.35	34.1	362	5.20	17.1	0.09	
0.60	4.40	32.8	372	5.20	16.9	0.09	
0.40	4.48	34.8	348	5.05	16.7	0.10	
0.20	4.58	36.5	343	4.70	16.7	0.11	
Unamended	4.70	37.1	333	4.45	16.6	0.11	
2.00	4.85	36.2	321	4.30	16.4	0.11	
4.00	5.30	31.3	310	4.27	16.4	0.10	
6.00	5.80	27.2	330	4.20	16.3	0.08	
8.00	6.25	21.7	327	4.20	15.4	0.06	
10.00	6.70	20.6	274	4.10	15.6	0.07	
20.00	7.95	15.2	220	4.02	15.1	0.07	
30.00	8.40	12.9	202	4.30	14.3	0.06	
40.00	8.60	12.8	211	4.40	12.6	0.06	
50.00	8.63	14.4	213	4.60	12.9	0.07	

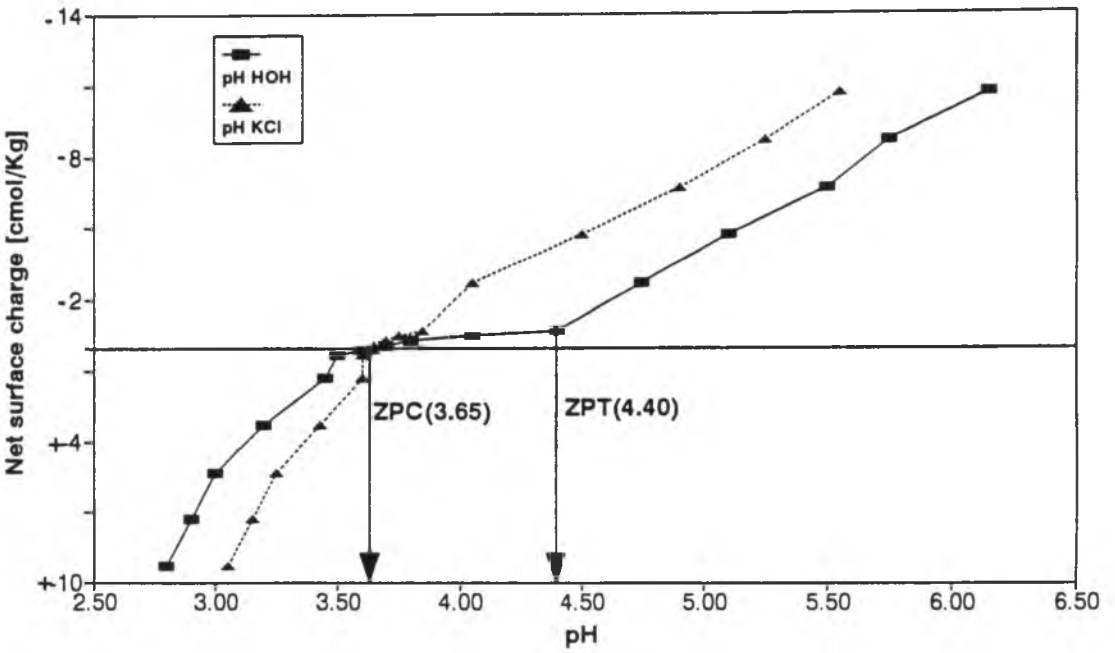

Fig 3.1. Net surface charge of the Paaloa Ultisol as a function of pH

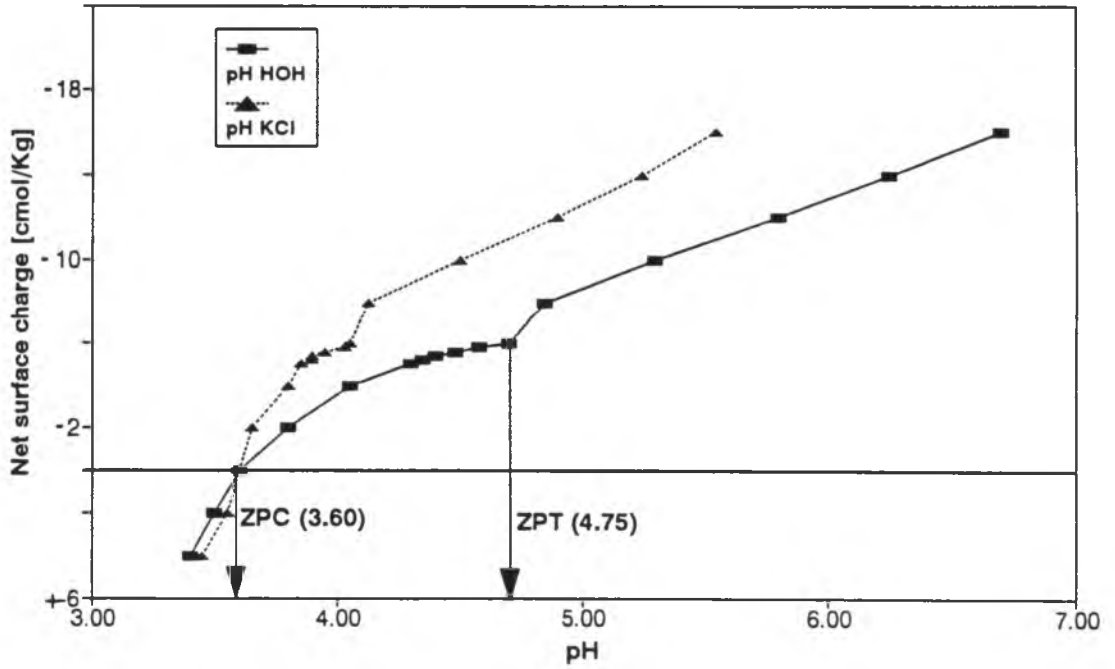

Fig 3.2 Net surface charge of the Wahiawa Oxisol as a function of pH

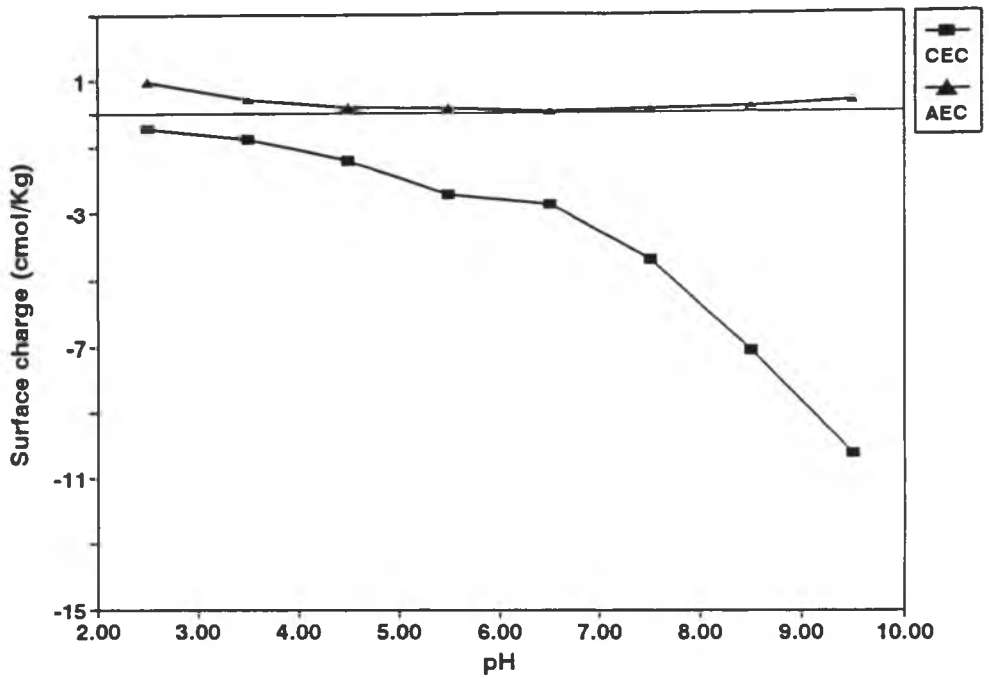

Fig 3.3 Variation of positive (AEC) and negative (CEC) charge in the Paaloa Ultisol as determined by the ion adsorption method

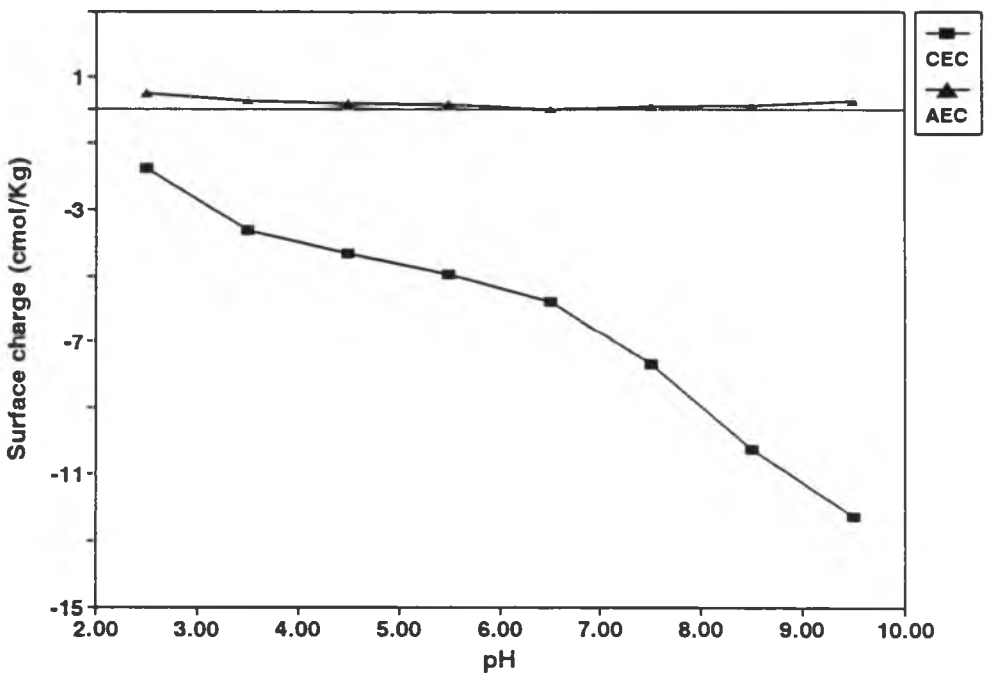

Fig 3.4 Variation of positive (AEC) and negative (CEC) charge in the Wahiawa Oxisol as determined by the ion adsorption method

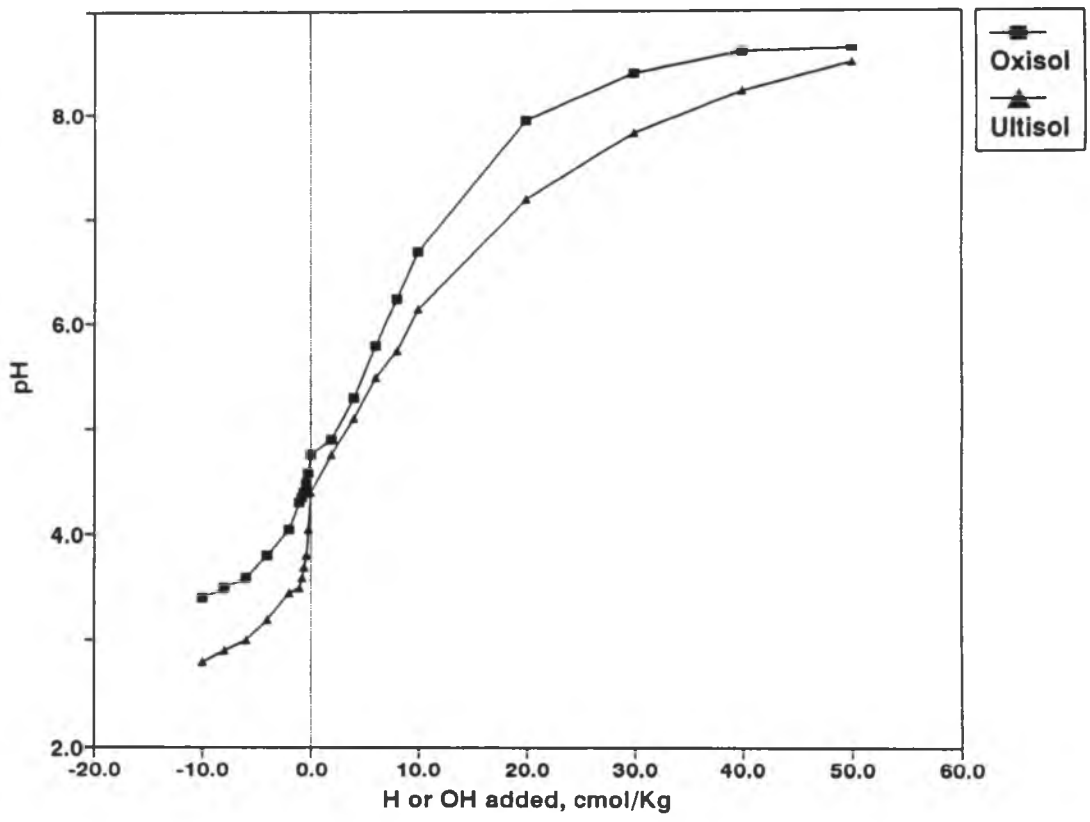

Fig 3.5 Acidification and lime titration curve of the Wahiawa Oxisol and the Paaloa Ultisol

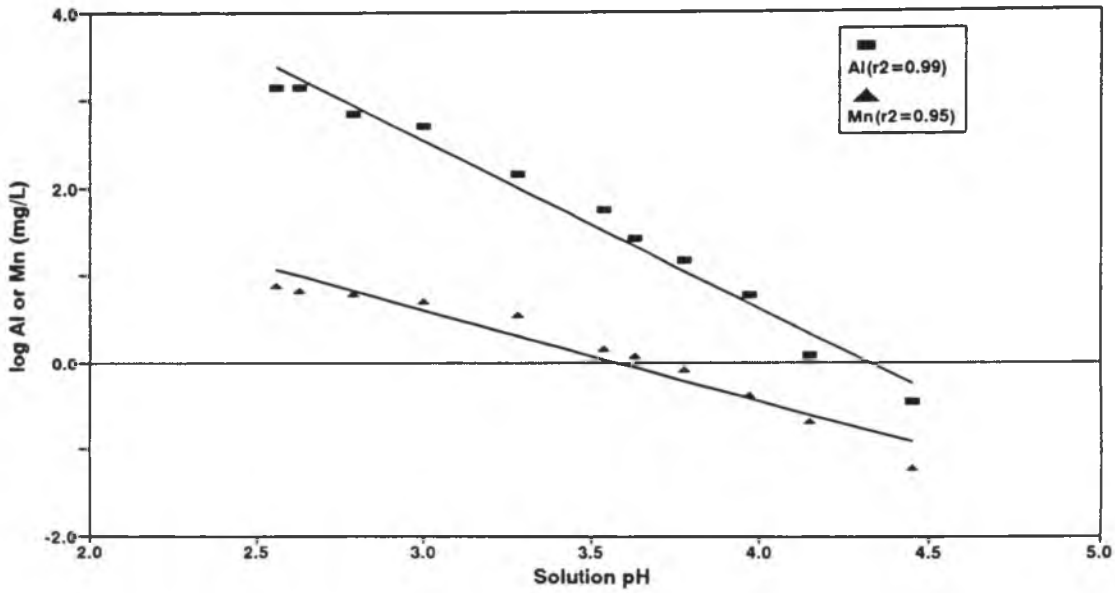

Fig 3.6 Relationship between pH and solution Al and Mn in the Paaloa Ultisol

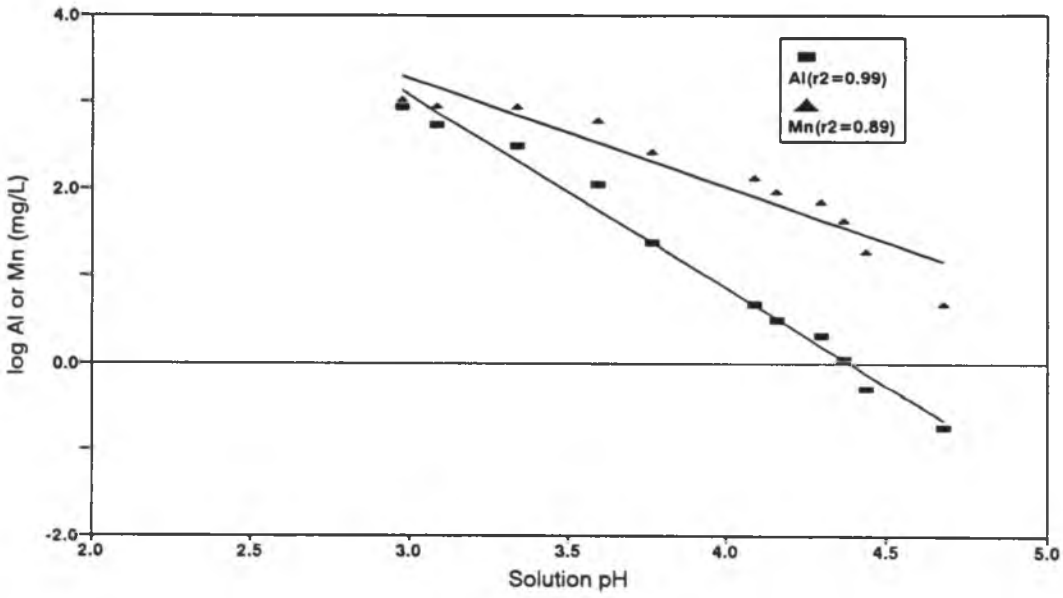

Fig 3.7 Relationship between pH and solution Al and Mn in the Wahiawa Oxisol

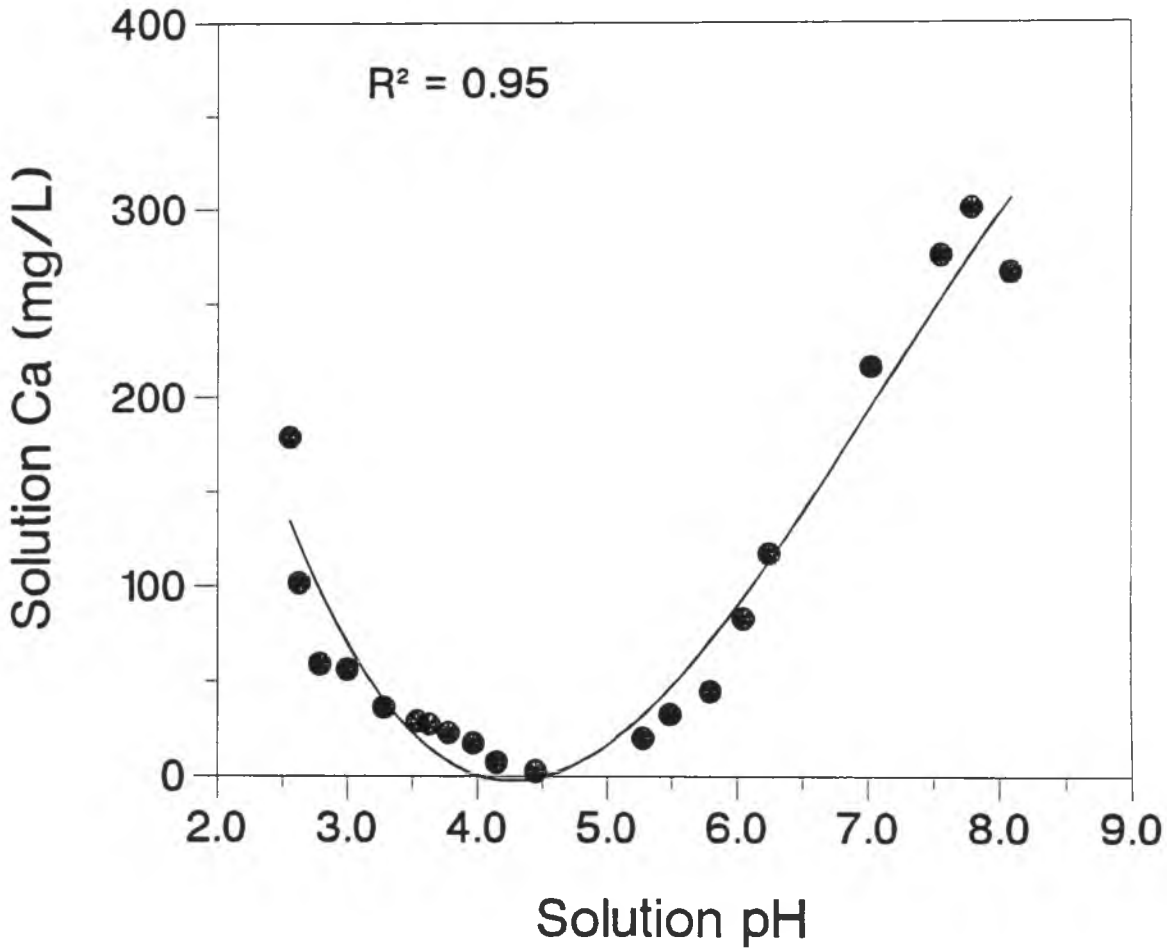

Fig 3.8 Relationship between pH and solution Ca in the Paaloa Ultisol

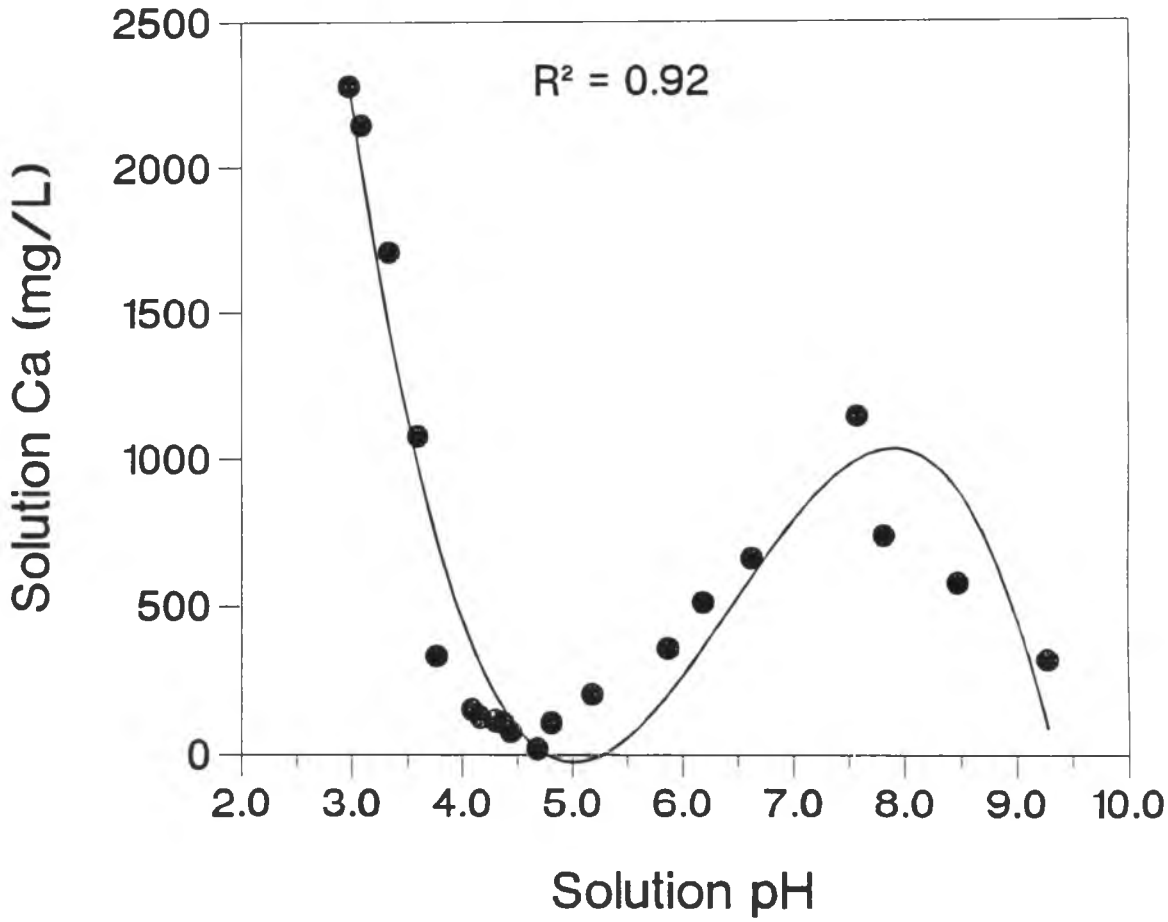

Fig 3.9 Relationship between pH and solution Ca in the Wahiawa Oxisol

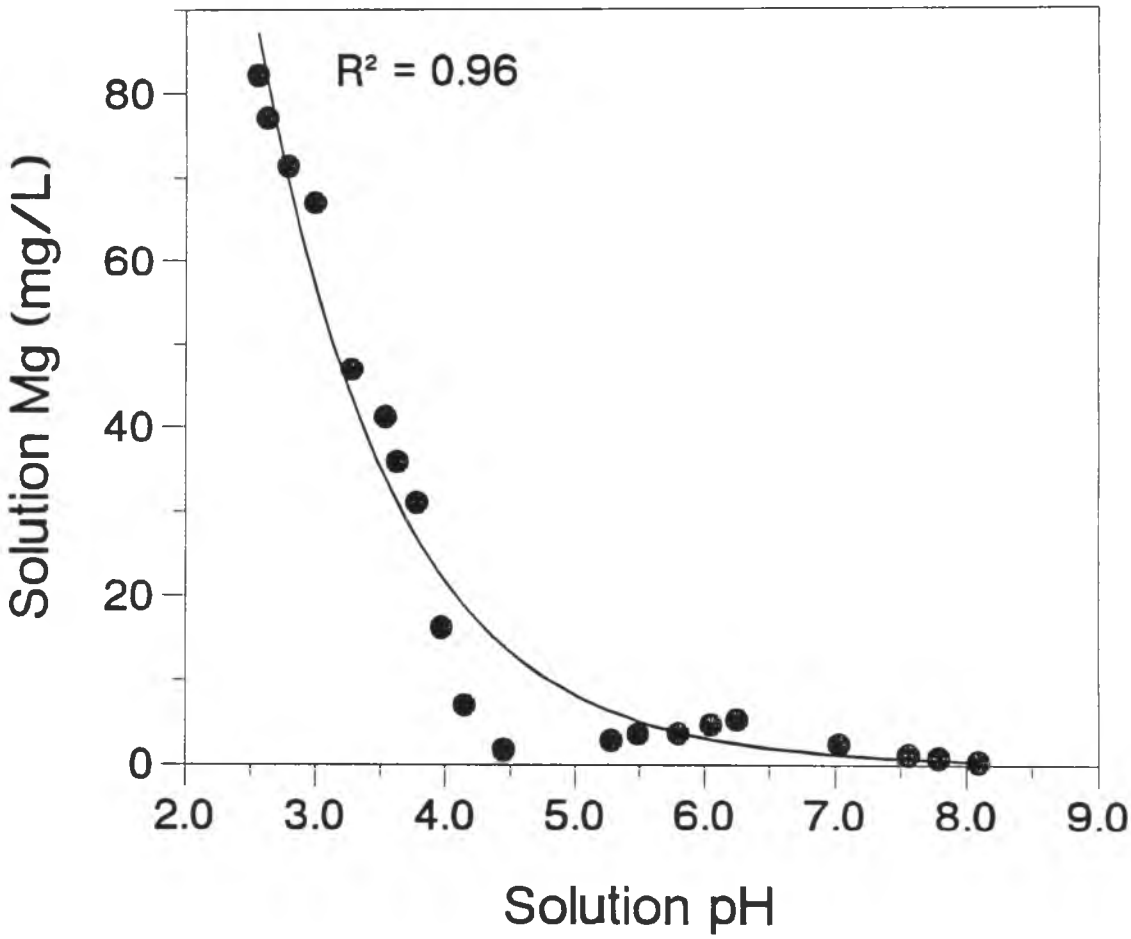

Fig 3.10 Relationship between pH and solution Mg in the Paaloa Ultisol

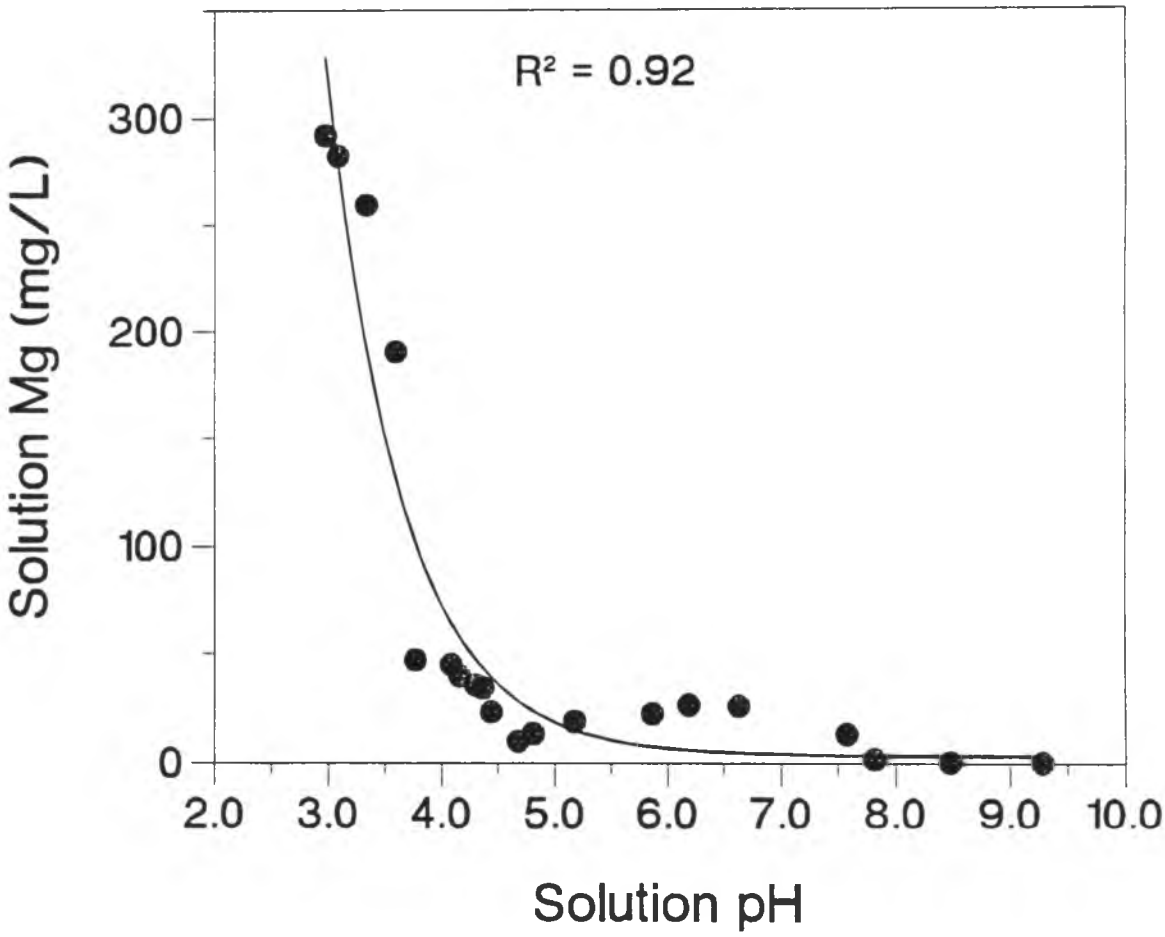

Fig 3.11 Relationship between pH and solution Mg in the Wahiawa Oxisol

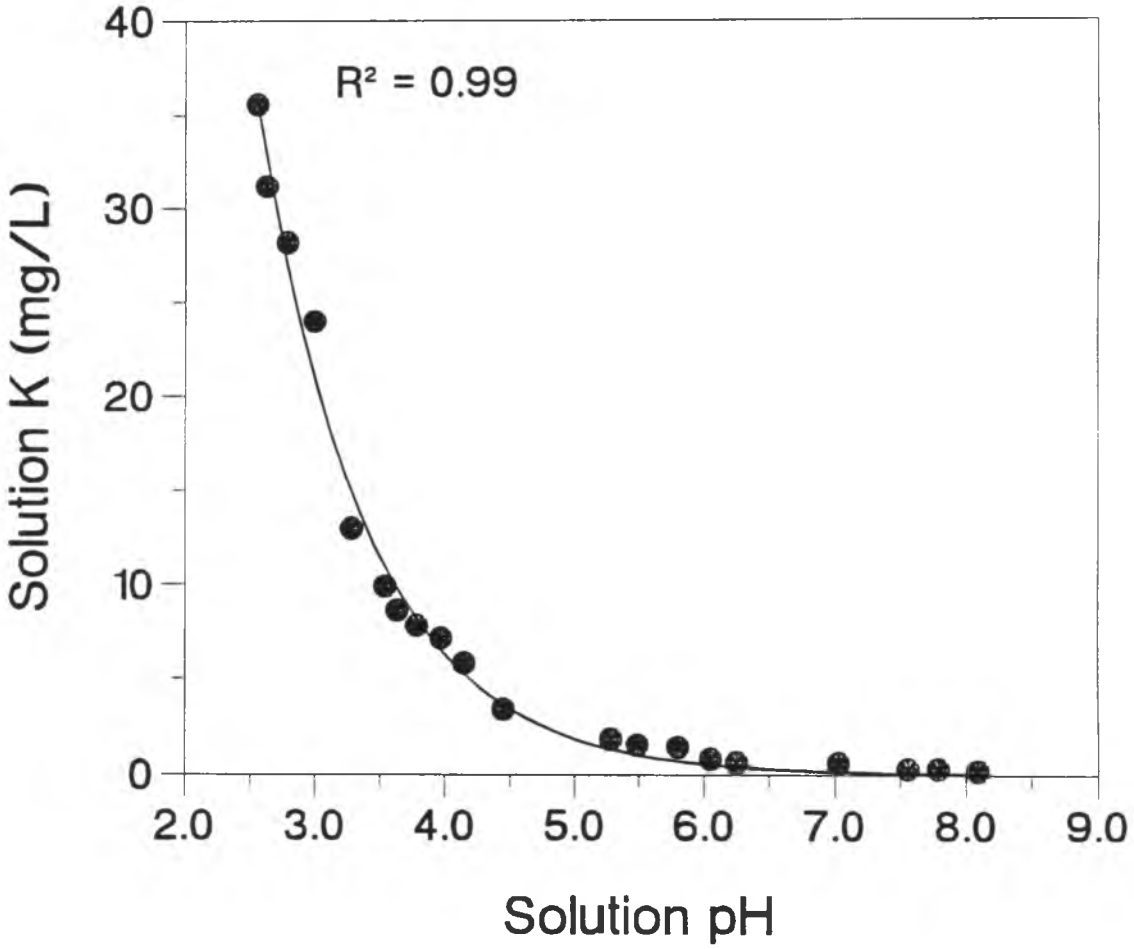

Fig 3.12 Relationship between pH and solution K in the Paaloa Ultisol

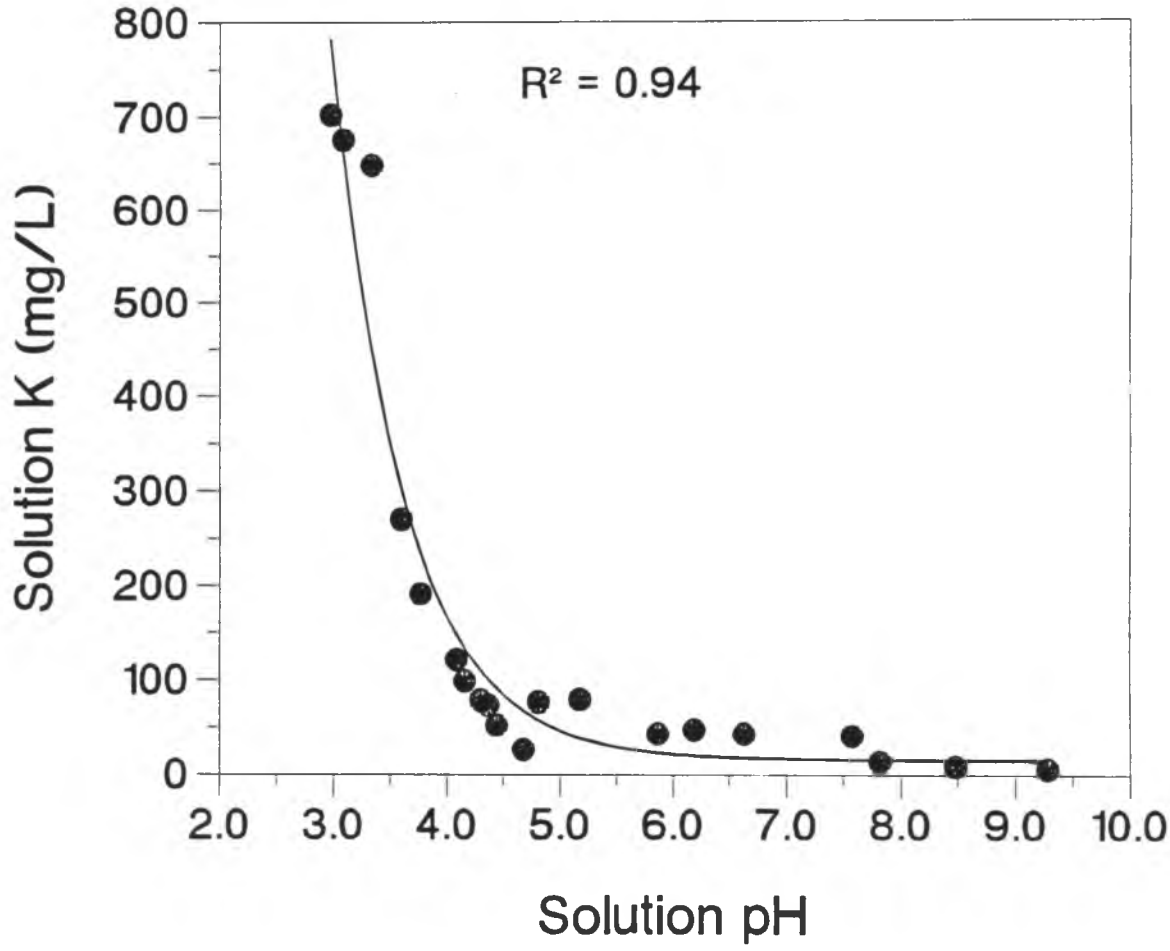

Fig 3.13 Relationship between pH and solution K in the Wahiawa Oxisol

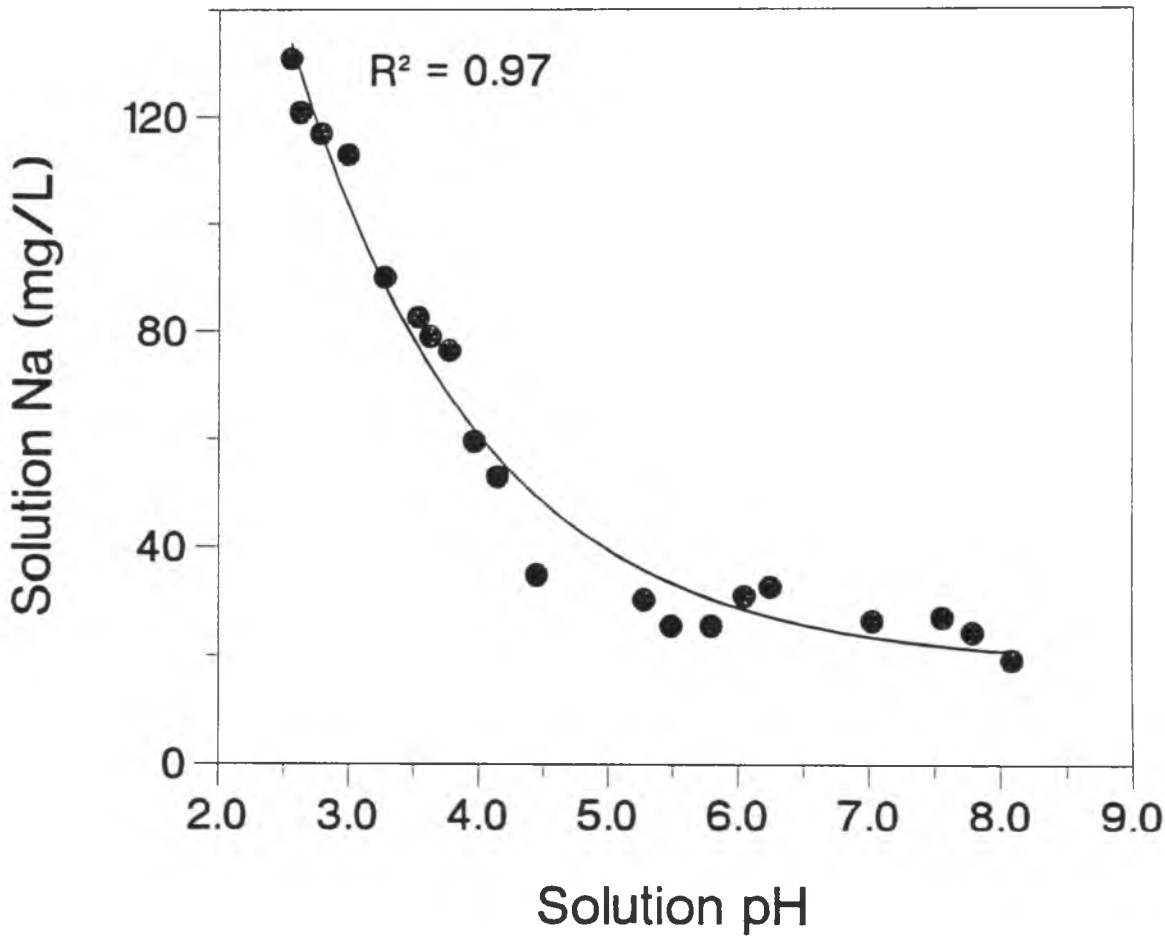

Fig 3.14 Relationship between pH and solution Na in the Paaloa Ultisol

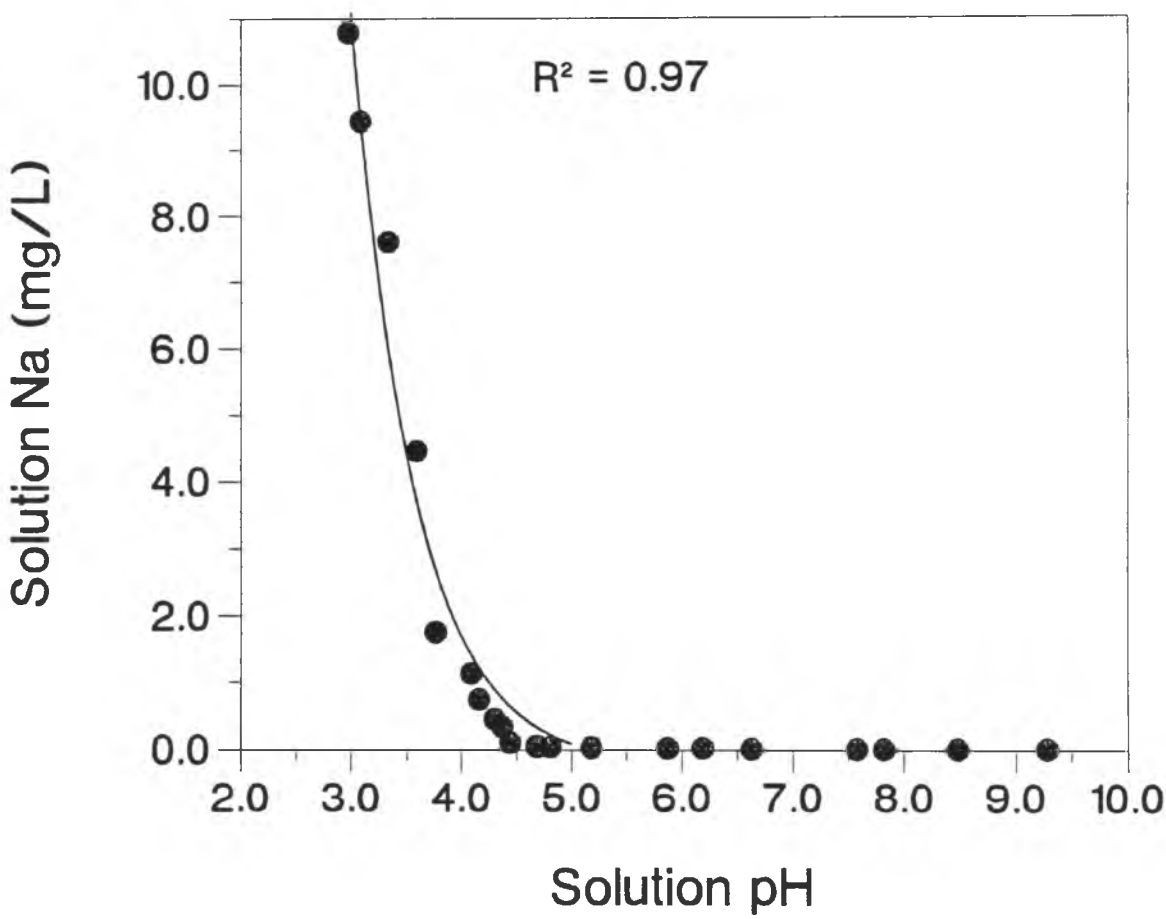

Fig 3.15 Relationship between pH and solution Na in the Wahiawa Oxisol

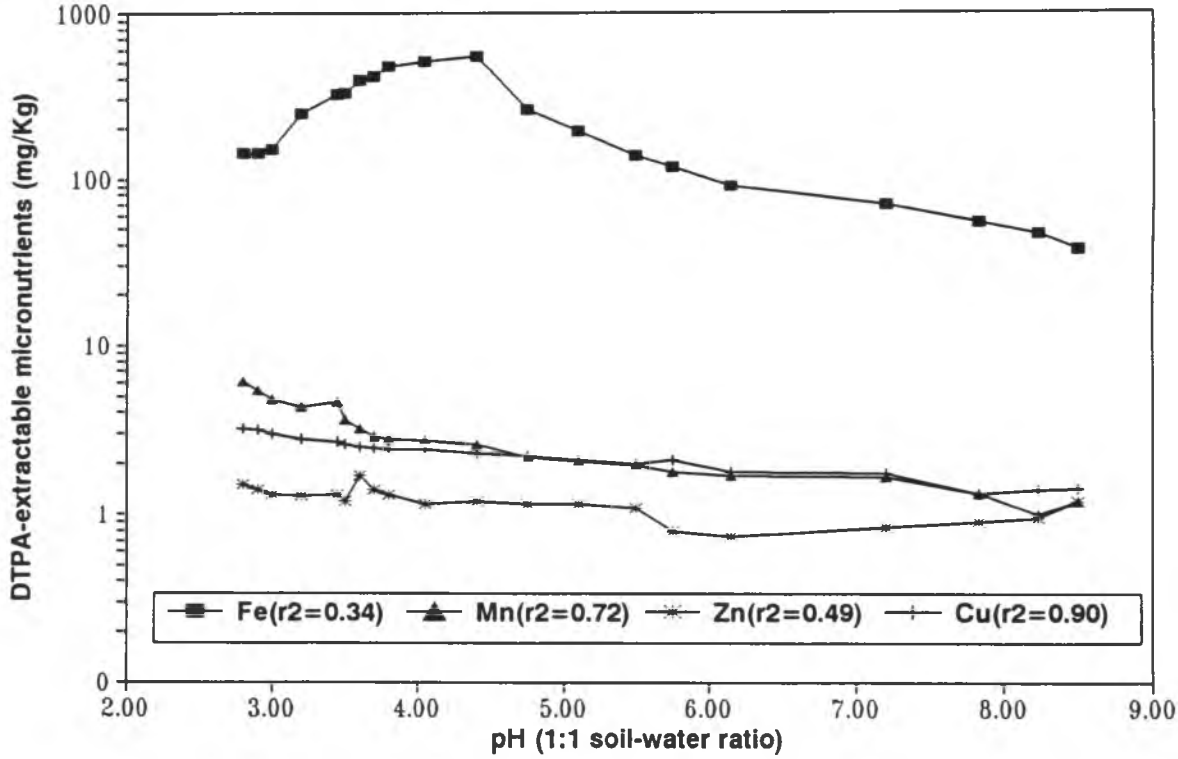

Fig 3.16 DTPA-extractable Cu, Fe, Mn, and Zn in the Paaloa Ultisol as affected by soil pH.

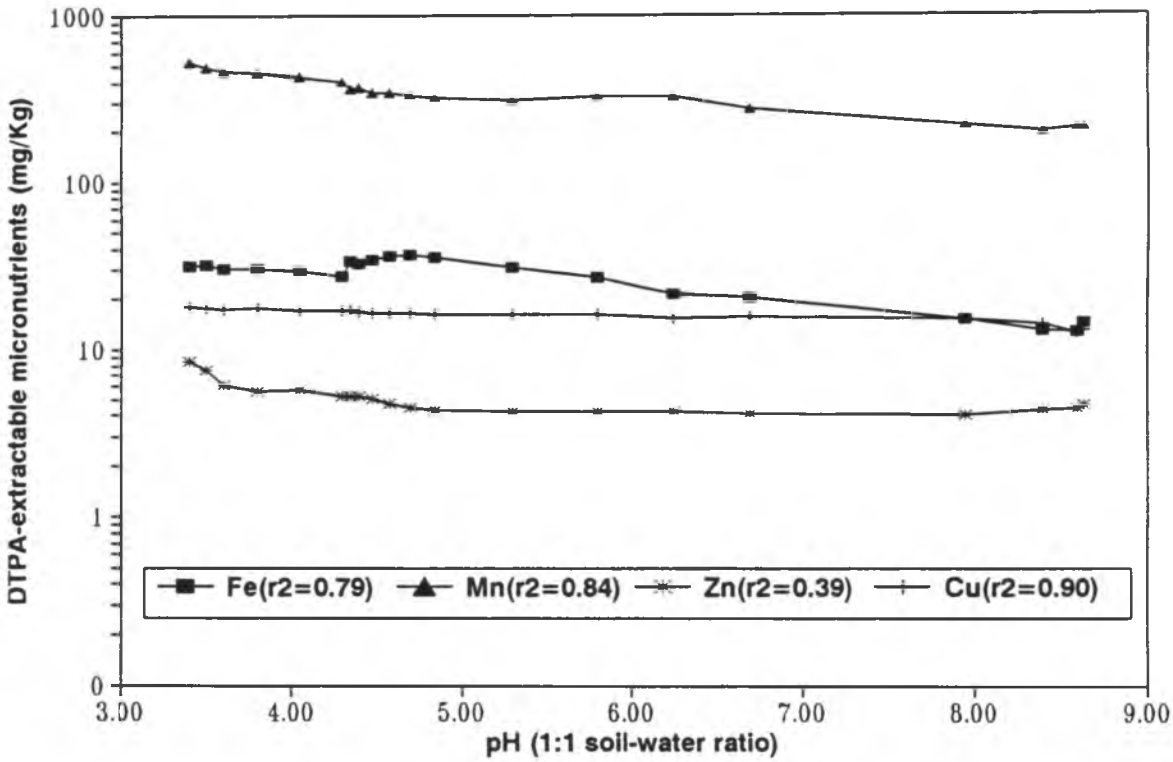

Fig 3.17 DTPA-extractable Cu, Fe, Mn, and Zn in the Wahiawa Oxisol as affected by soil pH.

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CHAPTER 4

EFFECT OF ORGANIC AMENDMENTS ON HIGHLY WEATHERED SOILS AT DIFFERENT pH LEVELS AS MEASURED BY SOYBEAN GROWTH

ABSTRACT

A hypothesis that organic manures can alleviate toxicity in acid soils, increase P availability in adequately limed soils and make micronutrients more available in over-limed soils was tested in a greenhouse experiment. To cover the diversity of factors limiting growth in acid soils, three soil materials from Hawaii were selected: an acid Oxisol high in Mn but low in Al, an acid Ultisol high in Al but low in Mn and Ca, and a mixture (1:1 by weight) of the two soils to simulate a soil that is both Al and Mn toxic. Three pH ranges of 4.0-5.0, 6.0-7.0, and 7.5-8.0 were established for each soil by either leaching with dilute HCl or adding $Ca(OH)_2$. Subsequently, ground leaves of cowpea (Vigna unguiculata) were mixed thoroughly with the soils at 0, 5, and 10 g Kg^{-1} for each pH range. Soils of the lowest pH received three additional treatments: an unamended control (no basal fertilizer) and sewage sludge at 5 and 10 g kg^{-1}. Inoculated soybeans (Glycine max L.) cv. Forrest were grown as a test crop. The results indicate that at low pH (pH 4.0-5.0), both green manure and sewage sludge decreased Al phytoxicity but increased Mn phytoxicity. At neutral pH, additions of the green manure did not increase phosphorus concentration in plants and soils, but

increased soil solution Ca, Mg, and K. At alkaline pH, Fe deficiency occurred in plants grown in all three soils; and additions of the green manure somewhat alleviated this deficiency.

INTRODUCTION

In acid soils, organic amendments, especially leguminous green manures and sewage sludges with low heavy-metal content have benefitted plant nutrition and soil fertility (Hue, 1992; Bessho and Bell, 1992). For example, crop residues, chicken manure, and sewage sludge have been used successfully to detoxify Al and soil acidity (Hue, 1992; Bessho and Bell, 1992; Lu and Hue, 1990). Major mechanisms of Al detoxification by organic amendments include increase in soil pH (Hue and Amien, 1989), displacement of exchangeable Al by basic cations (Bessho and Bell, 1992), and/or complexation of Al by organic compounds (Bartlett et al., 1991). Acid soils can also be Mn toxic, although less common (Fox et al., 1991). Given differences in the chemistry of Mn and Al, it is logical to ask if the effects of organic amendments would be as beneficial in Mn toxic soils as in Al-toxic soils.

In soils of neutral pH (6.0-7.0) the contributions of green manure to N nutrition are well recognized (Chae and Tabatabai, 1986), but for P and other plant nutrients the contribution is less clear-cut. Some studies (Sing et al., 1988; Tian et al., 1992) suggested that the availabilities of

P and other macronutrients (Ca, Mg, and K) might be significantly enhanced by organic amendments.

In soils that are naturally alkaline or have beeen over-limed, micronutrient deficiency, particularly Fe, is a common occurrence. Inorganic salts are not as effective in correcting such a deficiency because of precipitation, while certain organic wastes have shown promise (Chaney and Giordano, 1977; McCaslin et al., 1987).

OBJECTIVES

1. Evaluate the amendment effects of a cowpea green manure and a residential sewage sludge on Al and Mn toxicities in acid soils.

2. Evaluate the effect of green manure on plant P, $NaHCO_3$-extractable P, and solution Ca, Mg, and K in soils of neutral pH.

3. Evaluate the effect of a green manure on micronutrient availability in over-limed soils.

MATERIALS AND METHODS

SOIL MATERIALS

Three highly weathered soils from the island of Oahu, Hawaii were used in this investigation. The soils were an aluminous Ultisol (Paaloa series, clayey, oxidic, isothermic, Rhodic Kandiudults) low in Ca and Mn, a manganiferous Oxisol (Wahiawa series, clayey, kaolinitic isohyperthermic, Rhodic Eutrustox) low in Al, and a mixture (1:1 by weight) of the two

soils to simulate a soil that is both Al and Mn toxic. The Paaloa Ultisol is found at altitudes of 300 to 520 m and receives an average annual rainfall of 1750 and 2250 mm (Huang et al, 1989; Jackson et al., 1971). The Wahiawa Oxisol is found at altitudes of 300 to 350 m with an average annual rainfall of 1000 to 1250 mm (Jackson et al., 1971). Bulk soil samples were collected from the Ap horizon (0-20 cm) of the Oxisol and the Bt1 horizon (20-40 cm) of the Ultisol. All samples were air dried, and ground to pass a 6 mm sieve. Selected chemical and physical properties of the unamended soils are listed in Table 4.1

ORGANIC AMENDMENTS

Organic materials used consisted of a green manure of finely ground (<0.2 cm) cowpea leaves and an anaerobically digested sewage sludge from Kailua, Hawaii. Plant nutrient contents of the manures are listed in Table 4.2. Heavy metal contents of the sludge are within the limits set by the US Environmental Protection Agency (Hue and Ranjith, 1993).

BASAL FERTILIZERS

The soils received a blanket fertilizer treatment of (mg kg^{-1}): 140 (N), 200 (Ca), 48 (Mg), 160 (S), 10 (Fe), 5 (Cu), 5 (Zn), 2 (B), and 0.5 (Mo). The Ultisol also received 10 mg Mn kg^{-1}. N was applied as Urea. Ca, Mg, Fe, Cu, Zn, Mn and S were applied as sulfate salts. B was applied as H_3BO_3 (Boric acid) and Mo as Na molybdate. Based on P sorption isotherms (Hue,

1991), the Ultisol received in mg kg^{-1}; 400 P and 500 K, the Oxisol 200 P and 250 K, and the mixed soil 300 P and 375 K as KH_2PO_4.

PLANT MATERIAL

Soybean (Glycine max) cv. FORREST (maturity group = V), were used as a test crop. This genotype is sensitive to both Al and Mn toxicity (C. Foy, personal communication) and has been considered an Fe inefficient cultivar (Brown and Jones, 1977).

GREENHOUSE EXPERIMENTAL SETUP

A greenhouse experiment was conducted to study the effects of organic amendments on soil and plant composition at different pH levels. Three pH ranges of 4.0-5.0, 6.0-7.0, and 7.5-8.0 were established for each soil by either leaching with dilute HCl or $Ca(OH)_2$ based on the soil acidification and lime titration curve. After acidification or liming, all samples were moistened to field capacity. The soils were then subjected to two wetting-drying cycles, each consisted of a 3-day wetting followed by a 4-day drying. After equilibration, the soils were screened to pass a 6-mm sieve and placed in 2-kg plastic pots.

To quantify the effect of organic manures (and perhaps of basal fertilizers) on Al and Mn availability and phytoxicity, soils of the lowest pH (4.0-5.0) were subjected to six different treatments: an unamended control with no basal fertilizers (control-BF), a control with basal fertilizers

(control+BF), and 2 green manure and 2 sludge rates (5 and 10 g kg^{-1}). All the manure-amended soils received basal fertilizers. The soils were then moistened to field water holding capacity. To quantify the effect of the green manure on P phytoavailability as well as on soil solution Ca, Mg, and K, soils of the neutral pH (6.0-7.0) were thoroughly mixed with 0, 5, and 10 g kg^{-1} of ground cowpea leaves. Basal fertilizers were then added; and the soils were moistened to field capacity. Over-limed soils (pH 7.5-8.0) were treated in the same manner as those of neutral pH. Treated soils were subjected to two more cycles of wetting-drying. After equilibration, five soybean seeds were planted in each pot containing 2 kg of soil. The seedlings were thinned to two per pot 5 days after emergence. Deionized water was added daily to replace evaporation and to keep the soil near field-water-holding capacity. The pots were arranged in a completely randomized design with three replicates per treatment. The experimental design resulted in a total of 108 observations: 54 observations for the low pH (3 soils * 6 treatments * 3 reps) and 27 observations for each of the middle and high pH (3 soils * 3 treatments * 3 reps). Seedlings were harvested by cutting at the ground level 22 days after seeding for dry matter measurement and chemical analysis. The lenght of plant roots in the low pH treatments (4.0-5.0) was measured, then roots were washed free of soil, dried, weighed and analyzed

for Al and Mn. Soil samples were collected at planting and at harvest for chemical analysis.

LABORATORY ANALYSIS

The soil physical properties such as particle density, bulk density, porosity, and particle size distribution were measured following the procedures outlined by Gowland (1981).

Soil solution collection

Unaltered soil solutions were collected by a centrifugation method (Adams et al., 1980) for chemical characterization. In this method, approximately 250 g of moist soil (at field water holding capacity) was packed into a modified plastic Buchner funnel lined with a Whatman no. 42 filter paper. The whole assembly was centrifugated at 500 g for 30 minutes. Solution pH and electrical conductivity were measured immediately to avoid significant CO_2 loss. Thereafter, the soil solution was refrigerated for later chemical analysis.

Extraction procedures and chemical measurements

Exchangeable Ca, Mg, K, and Na were extracted with the same procedure used to determine CEC (Thomas et al., 1982). Extractable Al, Ca, Mg, and Na were extracted with 1M KCl (Shuman and Duncan, 1990). Effective CEC was calculated by summation of bases extracted by the neutral 1M NH_4OAc and 1M KCl extractable Al. Micronutrients (Fe, Cu, Zn, and Mn) were extracted with 0.01 M DTPA-TEA pH 7.3 solution (Lindsay and Norvell, 1978). Phosphorus was extracted with 0.5 M $NaHCO_3$ solution and determined by the sulpho-molybdate/ascorbic acid

method (Olsen and Sommers, 1982). Soil pH in 1M KCl and in H_2O were measured using a soil suspension ratio of 1:1. Soluble oxidizable organic carbon was determined with Mn (III)-pyrophosphate method (Barlett and Ross, 1988). Ca, Mg, K, Na, Fe, Cu, Mn, and Zn were determined with atomic absorption spectrophotometry. Total and monomeric Al concentrations in the soil solution were determined by the method of Kerven et al. (1989). Al in plants was determined by the method of Wilson (1984). Plant samples were dry-ashed at 500^0C; the residue was oxidized with HNO_3 and then dissolved in 0.1 M HCl. Plant nutrient composition was analyzed by the methods described above.

STATISTICAL ANALYSIS

Statistical analysis of soils was performed on average values of soil solution composition at planting and at harvest. Means among treatments were separated using the LSD test at 5% probability following an analysis of variance performed by PROC ANOVA of the Statistical Analysis System (SAS Institute, Inc., 1985).

RESULTS AND DISCUSSION

Effect of organic amendments and basal fertilizers on root growth and composition at low pH

The effects of organic amendments and basal fertilizers on soybean root growth and composition are shown in Table 4.3. Accompanying statistical analysis is shown in Appendix A. In

the Paaloa Ultisol, where Al toxicity was a growth limiting factor, basal fertilizers decreased root Al and increased root weight and root length. For example, root Al decreased from 8790 mg kg^{-1} in the control-BF to 6315 mg kg^{-1} in the control+BF, root weight increased from 0.028 g to 0.045 g, and root length from 4.1 cm to 10.3 cm, respectively. The ameliorative effect of added salts on root length of soybeans was also reported by Blamey et al. (1983). Applications of organic residues were even more effective than basal fertilizers in decreasing root Al concentration and increasing root weight and root length. For example, the application of 10 g kg^{-1} of cowpea leaves decreased root Al concentration from 6315 mg kg^{-1} (control+BF) to 2375 mg kg^{-1}, and increased root weight from 0.045 g to 0.29 g. Root lengths were also significantly increased by organic amendments, reaching a maximum value of 25.3 cm at the highest cowpea rate. At the same application rate, the green manure was more effective than the sewage sludge in increasing root weight and root length. Roots grown in the control-BF were in an advanced stage of Al injury. They were stubby, swollen, dark brown, and rough; indicating epidermis and cortex deterioration (Hutchinson et al., 1986). Roots became progressively less stunted as the Al content in the root decreased with organic amendments and/or fertilization.

A better linear relationship was obtained between root length and root Al (r^2=0.94) than between root weight and root

Al (r^2= 0.50). Thus, root length seems to be a better predictor of Al toxicity (Alva et al., 1986; Miyasaka and Webster, 1993). Recently, Mc Quanttie and Shier (1990) reported that although root weights of red spruce grown under different Al concentrations were not significantly different among treatments, root lengths were. Under Al stressed conditions roots increased considerably in diameter and their weights increased (Mc Quanttie and Shier, 1990).

Contrary to root Al concentration, root Mn concentration in the Paaloa Ultisol increased with organic amendments. Higher root Mn concentration in the green manure treatments is related to high Mn concentration in the green manure (Table 4.2).

In the Wahiawa Oxisol, where Mn toxicity was potentially toxic, fertilization decreased root Mn concentration, and increased root weight and length as compared to the control-BF. Decreased root Mn concentration seemed to be associated with increasing soil pH after basal fertilizer application (will be discussed later). Contrary to the effect of basal fertilizers, organic amendments increased root Mn and decreased root weight and length. For example, the application of 10 g kg^{-1} of sewage sludge and cowpea leaves increased root Mn concentration to 916 and 962 mg kg^{-1}, respectively from 739 mg kg^{-1} in the control+BF.

Unlike Al toxicity, Mn toxicity does not affect the root tips primarily but spreads more evenly throughout the root

systems. Therefore, root lengths may not be severely affected, unless large amounts of organic residues are applied. The results also indicate that Forrest soybean grown on manganiferous soil can accumulate high levels of Mn in roots. In fact, Loneragan (1988) reported that root Mn can be higher than shoot Mn when abundant Mn was supplied. High root Mn concentrations were also reported by Aoba (1986). This author found that roots of apple and persimmon trees can accumulate approximately 1200 and 2800 mg Mn kg^{-1} of Mn from a supply of 5 mg Mn L^{-1}. Root Mn concentration was expectedly much higher in the Oxisol than in the Ultisol. Root Al concentration in the Wahiawa Oxisol decreased with basal fertilizer and organic amendments additions.

In the Ultisol/Oxisol mixture, where both Al and Mn toxicities were moderate, application of basal fertilizer significantly decreased root Al and root Mn and increased root weight and root length. Organic amendments decreased root Al, but significantly increased root Mn concentration. Consequently, root weight was apparently unaffected by the organic amendments. Increased root weight in the green manure treatments, however, was probably due to lower Al content in the roots.

Relative root growth among the three soils was worth noting. For example, root weight of plants grown in the controls (-BF and +BF) of the mixed soil is higher than that of plants in the controls of the Ultisol and Oxisol.

Apparently mixed soils improved root weight. A similar pattern was observed for root length. For example, root lengths in the control-BF were 4.1, 23, and 18 cm for the Ultisol, Oxisol, and the mixed soil, respectively. Although root length increased considerably in the mixed soil as compared to the Ultisol, it was still lower than that in the Oxisol, suggesting the presence of Al toxicity.

Effect of organic amendments and basal fertilizers on shoot growth and nutrient composition of soybeans grown on low pH soils

Shoot dry weights and chemical composition of soybeans grown in low pH soils are listed in Table 4.4. Appendix B outlines the corresponding analysis of variance. Plant dry weight and chemical composition were statistically analyzed separately for each soil because of strong interactions between soils and fertilization treatments (Appendix B). In the Al-toxic Ultisol, organic amendments decreased slightly shoot Al concentrations and increased dry weights. Shoot weights were small and similar among the control-BF, the control+BF, and the 5 g kg^{-1} of sludge. In fact, the vegetative stage of plants grown in these 3 treatments was similar, having only the cotyledons, and small, necrotic unifoliate and trifoliate leaves. This suggests that the additions of basal fertilizers and 5 g kg^{-1} of sludge were not sufficient to overcome Al toxicity in the Ultisol. The high rate of sludge (10 g kg^{-1})

and both rates of the green manure, however, increased shoot weight significantly, indicating that Al toxicity in Forrest soybeans was decreased by these treatments. Compared to root Al, however, shoot Al was very low. For example, the highest shoot Al concentration (50 mg kg^{-1}) in the control-BF treatment was far below the 8792 mg kg^{-1} found in the corresponding roots (Table 4.3). This indicates that Al susceptible plants may accumulate large amounts of Al in roots, which can not be translocated to shoots (Rhue, 1977).

Shoot Al concentration seems to be a poor indicator of Al toxicity. For example the addition of 10 g kg^{-1} of the green manure decreased shoot Al by 9 mg kg^{-1} from the control-BF treatment. For comparison, corresponding root Al was decreased by 6500 mg kg^{-1} (Table 4.3).

Fertilization and organic amendments increased Ca uptake significantly compared to the control-BF. For example, shoot Ca increased from 0.37 % in the control-BF to 0.44 % in the control+BF and 0.54 % at the highest rate of the green manure. Green manure was more effective than sludge in increasing shoot Ca concentration, probably due to the higher Ca content in the manure (Table 4.2). Regardless of treatment, shoot Ca was below the critical deficiency level of 0.8 % reported for some soybean cultivars by Foy et al (1969) but was in the sufficient range (0.36%-2%) reported by de Mooy et al (1973) for youngest mature leaves of soybeans at late bloom. Foy et al. (1993), reported that the first trifoliate leaves of

Forrest soybeans grown in acid Tatum subsoil at pH 4.3 has a Ca concentration < 0.1 %. High Al in roots competes antagonistically with Ca for uptake and translocation, creating a potential Ca deficiency in plant shoots (Rengel, 1992). Soybeans grown in the control-BF, control+BF, and the 5 g kg^{-1} treatments of both manures had leaf distortion and petiole collapse. Although at 10 g kg^{-1} leaf distortion and petiole collapse still persisted, the problem was considerably less severe. Plants looked healthier and greener. According to Foy et al. (1991), petiole collapse and leaf distortion are typical symptoms of Al-induced Ca deficiency in soybeans.

Addition of basal fertilizers and organic manures also increased shoot Mg concentration. In all treatments, shoot Mg concentration was in the sufficient level (0.26 - 1 %), reported by de Mooy et al. (1973). Foy et al. (1993) reported that Mg concentration in the first trifoliate of Forrest soybeans grown in an Al-toxic subsoil was approximately 0.37 %.

Similar to Ca and Mg, application of basal fertilizers and organic residues significantly increased concentrations of shoot K, P, Fe, Cu, and Zn. Shoot Mn concentrations decreased with basal fertilizers and increased with organic amendments. Deficiencies of P, K, Mn, Fe, Cu, and Zn were not expected at low pH, because shoot concentrations of these elements were above the critical deficiency level outlined by de Mooy (1973) and Marschner (1989) for soybeans.

In the Mn-toxic Oxisol, addition of basal fertilizer decreased shoot Mn and increased shoot weight. Shoot Mn decreased from 2383 mg kg^{-1} in the control-BF to 1383 mg kg^{-1} in the control+BF; and shoot weights increased from 0.46 to 0.82 g. Manure additions, however, increased shoot Mn and decreased shoot weights relative to the control+BF treatment. For example, shoot Mn increased significantly from 1383 mg kg^{-1} in the control+BF to 1693 and 1886 mg kg^{-1} at 10 g kg^{-1} of sewage sludge and cowpea leaf addition, respectively. High shoot Mn concentrations decreased shoot weights from 0.82 g in the control+BF to 0.63 and 0.59 g at 10 g kg^{-1} of sewage sludge and cowpea leaf addition, respectively. Although plants grown in the control-BF were most affected by Mn toxicity, plants grown on all treatments had symptoms of Mn toxicity such as black and brown freckles on the cotyledons, the unifoliolate and trifoliolate leaves. Additionally, leaves were curled down with necrosis on leaf edges and tips, and ultimately became desiccated and shed. Small trifoliolate leaves were sometimes formed on the base of the cotyledon leaves. Besides these symptoms of Mn toxicity (Horst, 1988), older leaves were chlorotic with a distinct yellow color, and the youngest trifoliolate leaves were essentially white. This latter symptom has frequently been interpreted as Mn-induced Fe deficiency (Amberger et al., 1982). In fact, shoot composition (Table 4.4) indicates that Fe concentration in all treatments was below the 50 -150 mg kg^{-1} range suggested adequate for most

plants (Marschner, 1989). The higher Mn and lower Fe concentration in plants of the Wahiawa Oxisol than those of the Paaloa Ultisol, indicate that Mn-induced Fe deficiency might have been a limiting factor in the Oxisol.

The concentration of Ca, Mg, Cu, and Zn were also increased by basal fertilizers and organic amendments to the Oxisol. In the unamended state, the Oxisol is richer in cations than the Ultisol (Table 4.1); thus plants grown in the Oxisol contain higher concentrations of bases than those grown in the Ultisol. Shoot Al in the Oxisol was lower than shoot Al in the Ultisol. Shoot K and P concentration were similar in both soils.

In the mixed soil, where both Al and Mn may be toxic, basal fertilizer decreased shoot Al and shoot Mn. Therefore, shoot mass increased from 0.54 g in the control-BF to 0.72 g in the control+BF. Organic amendments increased shoot Mn concentration but decreased shoot Al concentration. Irrespective of treatments plants showed Mn toxicity symptoms such as curling leaves and freckles, and mild chlorosis. The beneficial effect from diluting Mn and Al levels by mixing soils is evident when the control-BF treatments were compared. For example, shoot weight in the unamended mixed soil (0.54 g) was higher than that in the unamended Ultisol (0.28 g) and in the unamended Oxisol (0.46 g).

Although the visual symptoms of plant grown in the mixed soil indicated Mn toxicity was predominant, Al toxicity would

have co-existed. In fact, Hue et al. (1987) have shown that Al uptake by macadamia leaves decreased considerably in soils high in Mn, probably due to Mn * Al interactions. To elucidate the nature of this interaction, however, further research would be needed.

Concentrations of shoot Ca, Mg, K, P, Cu, and Zn in the mixed soil were increased by basal fertilizers and organic amendments, the same pattern as in the Ultisol and Oxisol.

Effects of organic amendments increasing macro and micronutrient concentrations can be summarized as follows. The green manure was more effective in increasing shoot Mg, K, and Mn concentrations than the sewage sludge. The sludge, however, was more effective than the green manure in increasing shoot Fe, Cu, and Zn concentrations. Nutritional composition indicated that the sewage sludge contained more micronutrients while the green manure contained more macronutrients (Table 4.2).

Effect of organic amendments and basal fertilizers on soil composition

The effects of organic amendments and basal fertilizers on soil solution composition, KCl-extractable Al, and DTPA-extractable Fe, Mn, Cu, and Zn are shown in Tables 4.5 and 4.6. Analysis of variance for effects of soil types, treatments and their interactions on soil composition are shown in Appendix C. Because of similarities and for simplicity most soil chemical properties will be discussed

together for all three soils. Critical parameters such as pH, Al, Mn, Ca, and Fe contents will be discussed separately for each soil.

In the Al-toxic Ultisol, both the basal fertilizer and the organic manures significantly increased soil solution pH and decreased concentration of total and monomeric Al in the soil solution as well as KCl-extractable Al. For example, solution pH increased from 3.61 in the control-BF to 4.08 in the control+BF and to 4.39 and 4.45 in the 10 g kg^{-1} of sewage sludge and cowpea leaves, respectively. Monomeric soluble Al decreased from 42.5 mg L^{-1} in the control-BF to 2.82 mg L^{-1} in the control+BF, and to 0.69 mg L^{-1} and 0.43 mg kg^{-1} in the 10 g kg^{-1} of sludge and cowpea leaves, respectively. Similarly, KCl-extractable Al decreased from 2.8 $cmol_c kg^{-1}$ in the control-BF to 2.1 $cmol_c kg^{-1}$ in the control+BF and to 1.47 and 1.08 $cmol_c kg^{-1}$ in the 10 g kg^{-1} of sludge and cowpea additions. A linear relationship was found ($r2 = 0.93$) when soil solution pH was plotted against soluble monomeric Al concentration, indicating the pH-dependent nature of soluble Al. Increasing pH by basal fertilizer additions may have resulted from the exchange of phosphate and sulfate ions for OH^- on hydrous oxide surfaces (Uehara and Gillman, 1981; Matheus and Joost, 1989). Rises in soil solution pH through organic amendments were also reported by Hoyt and Turner (1975), Hue and Amien (1989), and Besho and Bell (1992). Hoyt and Turner (1975) suggested that NH_3 released from decomposition of organic residues increased soil

pH; and Hue and Amien (1989) proposed that pH increases due to the production of OH^- by (1) dissolution of Mn and Fe oxides in reducing environments or (2) ligand exchange reactions between organic anions and termal OH of sesquioxides.

Cowpea leaves were more effective than sewage sludge in increasing soil pH perhaps as a result of a quicker decomposition of the green manure (N.V. Hue, personal communication).

Similarities in the concentration of total and monomeric soluble Al in both control treatments, is intriguing and suggests that the natural organic matter content of the no-manured soil may have had a minor effect on Al complexation during the short term experiment. Applications of sludge and cowpea at 10 g kg^{-1} increased the difference between monomeric and total Al to approximately 15 %. Thus, fresh organic residues can complex more Al, probably due to the release of organic acids (Hue et al., 1986; Bessho and Bell, 1992). Bessho and Bell (1992) also reported that 10 g kg^{-1} of legume leaves applied to an acid soil from Australia yielded approximately a 10 % difference between total soluble and monomeric Al.

The decrease in KCl-extractable Al by organic amendments and basal fertilizer could result from an increased pH which precipitates Al as $Al(OH)_3$ (Bohn et al., 1985) and /or from complexation of Al by solid organic compounds (Ritchie, 1989).

A hyperbolic relationship was obtained when relative root

length (RRL) whas plotted against monomeric Al concentration (Fig 4.1). Root lengths of plants grown in the Ultisol at neutral pH were used as the maximum length. Fig 4.1 indicates that a 10 % reduction in root length of Forrest soybeans is expected when monomeric Al concentration is approximately 0.3 mg L^{-1}. This level is close to the critical value of 0.40 mg L^{-1} for monomeric Al concentration reported by Bruce et al (1988) for relative root length of Forrest soybeans.

Ca deficiency would be not expected in Ultisol because the lowest Ca concentration was 31 mg L^{-1} in the control-BF. The critical level of soluble Ca was reportedly 10.8 mg kg^{-1} for Alabama soils (Adams and Moore, 1983). Furthermore, the ratio of solution Ca to total Ca was always > 0.15, a ratio required for adequate root growth (Adams, 1966). Low Ca in shoots, therefore, may have been caused by Al interference with Ca accumulation in roots and decreased root surface area (Clarkson, 1984).

In the Mn-toxic Oxisol, application of basal fertilizers increased solution pH and decreased significantly soluble and DTPA-extractable Mn. In the control-BF solution pH was 4.55 and soluble Mn and DTPA-extractable Mn 154 mg L^{-1} and 316 mg kg^{-1}, respectively. With fertilizers (control+BF) soil pH increased to 4.93 and soluble Mn and DTPA-extractable Mn decreased to 83 mg L^{-1} and 264 mg kg^{-1}, respectively. Organic amendments further increased solution pH to 5.22 and 5.54 for the 10 g kg^{-1} of sludge and cowpea applications. The larger pH

increases in the Oxisol by inorganic and organic amendments as compared to the Ultisol, could be explained by the lower buffering capacity of the Oxisol.

Although organic amendments increased solution pH, they increased considerably soluble and DTPA-extractable Mn. For example, 10 g kg^{-1} of cowpea increased soluble Mn from 83 mg L^{-1} (in the control+BF) to 107 mg L^{-1} and extractable Mn from 264 to 297 mg kg^{-1}. Cowpea leaves were more effective than sewage sludge in increasing soluble and DTPA-extractable Mn. Earlier work has shown that organic amendments increased Mn concentration in the Wahiawa Oxisol (Fujimoto and Sherman, 1942; Asghar and Kanehiro, 1980; Hue, 1988; Vega et al., 1992).

Unlike Al, Mn is a transition element amenable to complex and redox reactions (Bartlett, 1988). Compared to other transition elements, ionic Mn^{+2} is a poor complexer, because only 1 electron is available in the d orbital for complex formation. Mn complexation, however, increases at higher pH due to increasing availability of ligands. At low pH, electrons derived from organic residue decomposition and abundance of H^+ may favor the dissolution of Mn minerals, and Mn availability, according to the following reaction.

$$MnO_2 \text{ (solid)} + 4\ H^+ + 2e^- = Mn^{+2} + 2H_2O \qquad [1]$$

High Mn concentration in the Oxisol decreased DTPA-extractable Fe concentration, as explained by the following equation (Hem, 1964).

$$2\ Fe(OH)_3 + Mn^{+2} + 2H^+ = MnO_2 + 4\ H_2O + 2\ Fe^{+2}$$

Similar to the Ultisol, monomeric and total soluble Al concentration as well as KCl-extractable Al in the Oxisol decreased with basal and organic amendment additions. Concentrations of Al in the Oxisol, however, were much lower than the Ultisol. By contrast, soil solution Ca was considerably higher in the Oxisol than the Ultisol.

In the mixed soil, where both Al and Mn are potentially toxic, soil solution pH increased from 4.28 in the control-BF to 4.58 in the control+BF and to 4.86 and 4.92 with the additions of 10 g kg^{-1} of sewage and cowpea leaves. Increasing soil solution pH decreased solution Al and KCl-extractable Al in all treatments. In general, the Al content in the mixed soils fell between those of the Ultisol and the Oxisol. Monomeric soluble Al in the control-BF of the Ultisol was considerably higher (44.8 mg L^{-1}) than 1.39 mg L^{-1} found in the mixed soil. However, the latter value was considerably higher than the critical level of 0.3 mg L^{-1} needed for a 10 % reduction in root length of plants grown in the Ultisol alone. It is intriguing, therefore, why this high concentration of monomeric Al was not as lethal as it was to plants grown in the Ultisol.

THe treatment effect on soluble Mn and DTPA-extractable Mn in the mixed soil followed the same trend as in the Oxisol; Mn content decreased with basal fertilizers but increased with organic amendments. In general, the concentration of both soil

solution and DTPA-extractable Mn in the mixed soil was about half of those in the Oxisol.

DTPA-extractable Fe and soil solution Ca in the mixed soil also fell in between extractable Fe and soil solution Ca concentrations in the Ultisol and the Oxisol.

In all three soils, electrical conductivity (EC) increased with basal fertilizer and organic amendments. For the same treatment, the Oxisol had higher EC than the Ultisol, probably due to higher concentration of soil solution cations in the Oxisol (Table 4.1). EC of the mixed soil was generally an average of the EC in the Ultisol and Oxisol.

Soluble oxidizable C and soil solution Na in all three soils were similar. Sludge amendments had slightly higher soluble C concentration and considerably higher Na concentration than treatments with cowpea green manure regardless of soil type.

In contrast to soil solution K, concentrations of soil solution Mg were higher in the Oxisol than in the Ultisol. Soil solution Mg and K in the mixed soil fell in between solution Mg and K in the Ultisol and Oxisol. Addition of green manure was more efficient in increasing K and Mg concentration than the sludge in all three soils. Higher concentrations of K and Mg in the cowpea leaves than in the sludge (Table 4.2) explained the results. DTPA-extractable Zn and Cu concentration was significantly increased by basal fertilizers and sewage sludge applications in all three soils, but was

unaffected by green manure additions. Higher concentrations of micronutrients in the sludge than in the green manure (Table 4.2) adequately explained the results.

Effect of green manure on plant growth and composition at neutral pH

The effect of cowpea additions on plant growth and composition at neutral pH is shown in Table 4.7. Corresponding analysis of variance is listed in Appendix D.

In the Ultisol, liming increased shoot weight considerably. The ameliorative effect of liming on plant growth can be estimated from shoot weights in the control+BF of the limed soils and the acid soils (compare Tables 3.4 and 4.7). Control+BF of the limed Ultisol produced 1.65 g/pot, approximately 5-fold higher than the same treatment in the acid soil (0.30 g/pot). Besides having greater biomass, plants grown in the adequately limed Ultisol were greener and more vigorous than plants grown under Al stress at lower pH.

The effect of green manuring on shoot weight and P concentration of plants grown in the neutral Paaloa Ultisol, however, was slight. Dry matter yields increased from 1.65 g to 1.74 g and 1.78 g when green manure was added at the rate of 0, 5, and 10 g kg^{-1}, respectively. Although the difference in the biomass production of the control and the highest level of green manure addition, was statistically significant, the increase was small. Shoot P concentrations increased slightly

from 0.13 % to 0.14 % and 0.15 % as application rates of organic manures increased from 0 to 5 and 10 g kg^{-1}. These increases were not statistically significant. The nearly constant P uptake suggests that factor (s) other than P from the manure was enhancing growth. Similar to P, concentrations of Ca, Mg, K, Mn, Fe, Cu, and Zn in shoot remained virtually unaffected by green manure additions. Although plant N was not measured, it was unlikely that N was deficient, because (1) 140 mg N kg^{-1} was added to all treatments as a basal fertilizer, and (2) soybean is a N fixing legume and no symptoms of N deficiency were observed at harvest. As claimed by Chen and Aviad (1990), the organic residues may have released some unidentified growth stimulants to the soil solution. These hormone-like compounds could increase biomass production without changing nutrient composition.

In the Oxisol, liming also considerably increased shoot weights (compare Tables 4.4 and 4.7). For example, shoot weight of plants grown in the control+BF of the limed soil was 1.71 g, approximately 2-fold greater than shoot weight (0.82 g) of plants grown in the same treatment of the acid soil. Contrary to lime, addition of green manure decreased shoot mass. For example, shoot weight decreased from 1.71 g to 1.43 g and 1.29 g per pot when green manures were added at 0, 5, and 10 g kg^{-1}, respectively. Shoot P concentration remained unchanged. Although Ca concentration decreased with increasing green manure additions, symptoms of Ca deficiency were absent

in all plants. Deficiency or toxicity of Mg, Cu, and Zn was unlikely because the concentration of these elements remained generally unchanged by green manure addition. The yield decrease seemed to be related to Mn toxicity and perhaps Fe deficiency. Leaves of plants grown in the 5 g kg^{-1} of manure had sporadic freckles on the unifoliolate and some older trifoliolate leaves (Mn toxicity) and slight chlorosis in the young trifoliolates (Fe deficiency). Leaves of plants grown in the 10 g kg^{-1} of green manure addition had numerous freckles and brown spots on the older leaves as well as distinct chlorosis in young trifoliates. Mn concentration increased from 176 mg kg^{-1} to 202 and 234 mg kg^{-1} and Fe concentration decreased from 99.7 mg kg^{-1} to 85.3 and 67 mg kg^{-1} as the manure rate increased from 0 to 5 and 10 g kg^{-1}. Since Forrest soybeans are highly susceptible to Mn toxicity (Brown and Jones, 1977), Mn toxicity might have occurred in this cultivar when shoot Mn is over 176 mg kg^{-1}. In fact, Brown and Jones (1977) observed Mn toxicity in Forrest soybeans when shoot Mn was as low as 58 mg kg-1.

In the mixed soil, liming also increased shoot weights considerably (compare Tables 4.4 and 4.7). For example, shoot weights of plants grown in the control+BF was 1.60 g, approximately two-fold greater than the shoot weight (0.72 g) of plants grown in the control+BF of the acid soil. In this mixed medium, plants grown in all levels of green manure addition were vigorous and green, indicating that the

increased growth in the Ultisol offset the decreased growth in the Oxisol. The net effect was little change in shoot weight regardless of the manure rates. Similar to shoot biomass, shoot P, Ca, Mg, K, Cu, and Zn concentrations remained practically unchanged, indicating that the uptake of these nutrients was not enhanced by green manure additions in this mixed medium. Although the concentration of shoot Mn was increased and shoot Fe was decreased by green manure additions, no symptoms of Mn toxicity or Fe deficiency were observed.

Effect of green manure on soil composition at neutral pH

The effects of green manure on soil composition is shown in Tables 4.8 and 4.9, respectively. Statistical analysis of these effects is shown in Appendix E.

In all 3 soils, solution pH, electrical conductivity, and soluble C increased significantly with increasing green manure addition. Green manure additions only slightly affected on the concentration of soil solution Na and DTPA-extractable Cu and Zn.

Soil solution Mn and DTPA-extractable Mn were considerably higher in the Oxisol. In the Wahiawa Oxisol soil solution Mn increased from 2.33 to 6.73 and 12.8 mg L^{-1} as the additions of green manure increased from 0 to 5 and 10 g kg^{-1}. Similarly, 10 g kg^{-1} of green manure increased soil solution Mn to 0.50 mg L^{-1} in the Ultisol and 4.3 mg L^{-1} in the mixed soil. Results indicate that shoot biomass of Forrest soybeans would

be reduced considerably when soil solution Mn is > 5 mg L^{-1}. Mascarenhas et al.(1985), however, reported that as little as 2 mg kg^{-1} of Mn in the nutrient solution was toxic to Forrest soybeans. Results also indicate that Mn toxicity can still occur in manganiferous soils at high pH if organic residues are added to the soils. This may be a potential problem if the soil is used to receive wastes for disposal. In Hawaii, for example, large amounts of undecomposed sugar cane and pineapple residues are added annually to the soils (Asghar and Kanehiro, 1980).

$NaHCO_3$ extractable P was largelly unaffected by green manure addition in the Ultisol and the mixed soil. In the Wahiawa Oxisol, however, addition of 10 g kg^{-1} of green manure increased P concentration from 45.7 mg kg^{-1} to 51.7 mg kg^{-1}. Given the low level boundaries of critical level for extractable P as 8 and 16 mg kg-1 (Olsen et al., 1954), P concentration were sufficient for plants grown in all three soils. The 6 mg kg-1 of extractable P released from the highest rate of green manure addition, however, may be important if the manures are added to unamended soils. The unamended Wahiawa Oxisol, for example, contains 5.5 mg kg^{-1} of extractable P (Table 4.1) which increased to 11 mg kg^{-1} with the application of 10 g kg^{-1} of the green manure.

Green manure increased soil solution Ca, Mg, and K in all three soils (Table 4.8). Soil solution Ca and Mg were considerably higher in the Oxisol than in the Ultisol and the

mixed soil. This difference was probably derived from the higher natural fertility of the Oxisol (Table 4.1). Although the unamended Oxisol was also richer in K than the unamended Ultisol (Table 4.1), K application from the basal fertilizer resulted in higher soluble K concentration in the Ultisol than the other two soils. Concentrations of soluble Ca, Mg, and K in the mixed soil always fell in between those of the other two soils. Table 4.10 shows the amount (mg kg^{-1}) of soluble Ca, Mg, and K released in all three soils by the additions of 5 and 10 g kg^{-1} of the cowpea manure. For example, soluble Ca levels released by the addition of 10 g kg^{-1} of the manure were 80, 81 and 96 mg kg^{-1} in the Ultisol, Oxisol, and the mixed soil, respectively. Given the critical deficiency level of 10.8 mg kg^{-1} of soluble Ca for Alabama soils (Adams and Moore, 1983), the addition of 10 g kg^{-1} of cowpea leaves will be more than sufficient to alleviate Ca deficiency in these soils. Results also indicate that more than 50 % of Ca in the green manure (Table 4.10) were mineralized during the experiment (< 2 months).

As for Mg, the addition of 10 g kg^{-1} of cowpea manure to the Ultisol, Oxisol, and the mixed soil released 12.1, 33.7 and 34 mg kg^{-1} of Mg into the soil solution, respectively. Results indicate that more than 90 % of Mg from the green manure (Table 4.10) were mineralized in the Oxisol and the mixed soil, but only approximately 32 % in the Ultisol.

Addition of 10 g kg^{-1} of green manure released 157, 63, and 89 mg kg^{-1} of soluble K in the Ultisol, Oxisol, and the mixed soil, respectively. Less than 50 % of the K present in the manure (Table 4.2) was mineralized in all three soils.

Results indicate that additions of cowpea green manure to soils significantly increase soil fertility. Thus, cowpea manure is a good organic fertilizer.

Effect of green manure on plant growth and composition on over-limed soils

The effects of cowpea manure on plant growth and composition in soils of alkaline pH are shown in Table 4.11. Corresponding statistical analysis is listed in Appendix F. In the Paaloa Ultisol, additions of 0, 5, and 10 g kg^{-1} of green manures increased shoot weights significantly from 0.57 g to 0.72 and 1.11 g per pot. Seedlings receiving 10 g kg^{-1} looked nearly normal. In contrast, the control plants were severely chlorotic and stunted; suggesting nutrient deficiency occurred. Macronutrient deficiency seemed improbable because they were added as basal fertilizers and tissue Ca, Mg, K, and P remained nearly constant. Given the critical deficiency level of Mn, Cu, and Zn in soybean leaves as 15, 4, and 10 mg kg^{-1} (de Mooy et al., 1973), these three micronutrients would be sufficient. On the other hand, increasing biomass production was strongly related to increasing tissue Fe concentration. Tissue Fe increased from 49.7 mg kg^{-1} in the no manured soil to 64.7 mg kg^{-1} at 5 g kg^{-1}, and 82.7 mg kg^{-1} at 10

g kg-1 of manure addition. Because Fe concentration in the manure was 500 mg kg^{-1} (Table 4.2), a total mineralization of this element would have released only 5 mg of Fe. This contribution would not be sufficient to explain the increment of 15 and 33 mg Fe kg^{-1} for plants grown at the rate of 5 and 10 g kg^{-1} of green manure as compared to the Fe content of the control plants. Increased Fe uptake appeared to be caused by the complexation of soil Fe by organic ligands released by the manure. Organically complexed Fe^{+3} can be adsorbed by the plasm membrane of the root cells (Marschner, 1989), then reduced to Fe^{+2} by a turbo mechanism (NADPH) that all dicot plants possess in their root epidermal cells (Bienfait, 1988). The resultant ferrous complexes can be translocated to the shoots (Bienfait, 1988). Additionally, it is possible that applications of the manure increased the siderophore (compound called Desferrioxamine B) input into the soil. Siderophores have been identified as a major complexer of Fe^{+3} (Marshner, 1989). Recently, Haselwandter et al (1988) reported that organic fertilizers such as chicken manures, and compost resulted in sufficient input of siderophores to alleviate Fe chlorosis in plants. The ameliorative effect of other organic amendments such as sewage sludge and farmyard manure on Fe nutrition of sorghum grown in calcareous soil has been reported (McCaslin et al., 1987; Matthers et al., 1980). Our results also indicate that Forrest soybean is an Fe inefficient cultivar, as first noted by Brown and Jones

(1977), when shoot weights in the control+BF of the over-limed and the adequately limed Ultisols are compared (Tables 4.4 and 4.11). For example, the over-limed treatment produced 0.57 g/pot, which is 65.5 % lower than 1.65 g/pot produced in the adequately limed Ultisol.

In the overlimed Wahiawa Oxisol, increases in shoot weight were also controlled by Fe availability. Both dry matter yields and Fe concentration increased slightly at 5 g kg^{-1}, and increased significantly with addition of 10 g kg^{-1} of manure. Compared to the Ultisol, manure amendments in the Oxisol were less effective. For example, 10 g kg^{-1} of the manure increased tissue Fe concentration by only 18 mg kg^{-1} in the Oxisol vs 33 mg kg^{-1} in the Ultisol. Therefore, chlorosis was detectable in all plants in the Oxisol, regardless of the treatments. Perhaps, the suggested Fe complexation mechanism was not as effective in the Oxisol. Furthermore, over-liming of the Oxisol decreased biomass production by 58 % when compared to the adequately limed Oxisol.

In the mixed soil, dry matter yields increased from 0.83 to 0.93 and 1.0 g/pot as the green manure additions increased from 0 to 5 and 10 g kg^{-1}. In general, Fe concentrations in plants grown in this mixed soil were higher than those in the Oxisol and the Ultisol, except for the highest rate of manure addition (10 g kg^{-1}) in which the Ultisol had higher Fe concentration (Table 4.11). All plants showed chlorosis. Plants grown in the overlimed mixed soil produced 48 % less

shoot biomass than plants grown in the adequately limed, mixed soil.

Effect of green manure on soil composition at alkaline pH

The effect of the green manure on soil composition is shown in Tables 4.12 and 4.13. Corresponding analysis of variance is listed in Appendix G. In all three soils, pH, EC, $NaHCO_3$-extractable P as well as soil solution C, Ca, Mg, K, and Na increased with increasing addition of cowpea manure. Behavior of soluble C and $NaHCO_3$-extractable P are worth noting. Soluble C and extractable P were higher in overlimed soils than in adequately limed soils. Alkaline pH can dissolve more organic materials and therefore soil solution C concentration may have increased at increasing pH. No explanation is readily available for increased extractable P. Considerably more P was extracted when green manure was added to the overlimed soils as compared to the neutral pH.

Although additions of the green manure significantly increased tissue Fe concentrations, DTPA-extractable Fe remained almost unchanged. These results indicate that Fe extracted by this method is a poor indicator of Fe availability. Given the Fe critical deficiency level for calcareous soil as 4.5 mg kg-1 (Lindsay and Norvell, 1978) the Fe in all three soils should not have been deficient, but deficiency symptoms did occur in soybean in all three soil.

SUMMARY AND CONCLUSIONS

In acid soils (pH 4.0-5.0)

* Both basal fertilizer and organic amendments (cowpea leaves and sewage sludge) were effective in reducing Al toxicity.

* Basal fertilizer decreased Mn toxicity, but organic amendments intensified it.

In neutral soils (pH 6.0-7.0)

* Organic amendments increased Mn toxicity in plants grown in the Oxisol, but produced no adverse effects on the Ultisol and the mixed soil.

* No distinct effects from organic amendments were observed on P concentrations in plants or soils.

* Soluble Ca, Mg, and K increased significantly with cowpea green manure additions, indicating that this material could be a good organic fertilizer.

In overlimed soils (pH 7.5-8.0)

* Cowpea green manure increased plant growth and Fe concentration in all three soils. Chlorosis was almost eliminated in the Ultisol with 10 g kg^{-1} of cowpea manure addition, but not in the Oxisol and the mixed soil. Perhaps a higher application rate of the manure would be needed to eliminate Fe deficiency.

* DTPA-extractable Fe did not reflect the green manure application.

Table 4.1. Selected chemical and physical properties of the soils used in the experiment.

	SOIL ORDER	
SELECTED PROPERTIES	Oxisol	Ultisol
1. CHEMICAL PROPERTIES		
1.1 GENERAL		
pH (1:1 soil:1M KCl)	4.30	3.90
pH (1:1 soil:H_2O)	5.30	4.40
Delta pH	-1.00	-0.50
Soil solution pH	5.30	4.65
Soil solut. EC, dS m^{-1} 0.66	0.25	
Soluble carbon, mg L^{-1}	90.5	74.6
CEC (NH_4AcO pH 7.0), $cmol_c Kg^{-1}$	10.4	7.93
Effective CEC, $cmol_c Kg^{-1}$	5.20	3.09
Base saturation, %	49.0	13.1
Al saturation, %	2.11	66.3
Total Mn, %	1.89	0.09
$NaHCO_3$ extractable P, mg Kg^{-1}	5.50	1.15
1.2 SOIL SOLUTION CATIONS (mg L^{-1})		
Ca	12.0	1.96
Mg	2.60	1.15
K	20.1	1.60
Na	14.9	12.5
Mn	2.50	0.13
Al	0.04	0.29
1.3 NH4OAc, pH 7.0 EXCHANGEABLE CATIONS	($cmol_c$Kg-1)	
Ca	2.40	0.37
Mg	1.71	0.21
K	0.74	0.10
Na	0.24	0.36
1.4 1 M KCl-EXTRACTABLE CATIONS ($cmol_c Kg^{-1}$)		
Ca	4.20	0.34
Mg	3.50	0.22
Na	0.43	0.30
Al	0.11	2.05
2.PHYSICAL PROPERTIES		
2.1 GENERAL		
Particle density, g cm^{-3}	2.86	3.12
Bulk density, g cm^{-3}	1.10	1.12
Porosity, %	62.0	63.0
Field water holding capac., %	38.0	34.0
2.2 PARTICLE SIZE DISTRIBUTION (%)		
Sand	4.30	2.20
Silt	46.2	48.2
Clay	49.5	49.6
Textural class	Silty clay	Silty clay

Table 4.2 Total nutrient contents of the manures used in this investigation.

	Major nutrients (%)				
Source	N	P	K	Ca	Mg
Cowpea leaves	3.60	0.41	3.45	1.54	0.37
Sewage sludge	5.35	0.79	0.01	0.35	0.35

	Minor nutrients (mg kg-1)				
	Cu	Zn	Mn	Fe	pH_{H20} (1:1)
Cowpea leaves	13	50	62.8	500	
Sewage sludge	416	1301	119	18935	6.58

Table 4.3 Root growth and composition of soybeans in the Ultisol, Oxisol, and the mixed soil as affected by basal fertilizer, green manure, and sewage sludge application at low pH.*

TREATMENTS	ROOT WEIGHT (g)	ROOT Al mg kg^{-1}	ROOT LENGTH (cm)	ROOT Mn mg kg^{-1}
		ULTISOL		
Control-BF**	0.028 d	8790 a	4.10 f	58.3 c
Control+BF	0.045 d	6315 b	10.3 e	64.7 cb
Sludge, 5 g kg^{-1}	0.049 dc	4697 c	13.1 d	80.7 b
Sludge, 10 g kg^{-1}	0.122 b	4208 c	17.9 c	82.5 b
Cowpea, 5 g kg^{-1}	0.083 c	4526 c	16.7 b	108 a
Cowpea, 10 g kg^{-1}	0.290 a	2375 d	25.3 a	114 a
Pr>F	0.0001	0.0001	0.0001	0.0001
		OXISOL		
Control-BF	0.064 c	2906 a	23.3 c	987 a
Control+BF	0.101 a	2133 b	29.9 a	740 c
Sludge, 5 g kg^{-1}	0.098 a	1960 c	30.0 a	753 c
Sludge, 10 g kg^{-1}	0.095 ab	1436 d	26.7 b	916 ab
Cowpea, 5 g kg^{-1}	0.087 b	1943 c	26.3 b	840 c
Cowpea, 10 g kg^{-1}	0.094 ab	1273 d	30.0 a	962 a
Pr>F	0.0001	0.0001	0.0006	0.0074
		MIXED SOIL		
Control-BF	0.096 a	4513 a	18.3 c	635 a
Control+BF	0.145 a	3233 b	24.0 b	376 c
Sludge, 5 g kg^{-1}	0.100 a	2700 c	23.3 b	366 c
Sludge, 10 g kg^{-1}	0.097 a	1517 e	26.0 b	490 b
Cowpea, 5 g kg^{-1}	0.145 a	2025 d	29.0 a	426 cb
Cowpea, 10 g kg^{-1}	0.193 a	1137 e	24.3 ab	613 a
Pr>F	0.2871	0.0001	0.0086	0.0001

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test
** BF= Basal fertilizer

Table 4.4 Shoot growth and composition of soybeans as affected by basal fertilizer, green manure, and sewage sludge applications at low pH.

TREATMENTS	DRY WEIGHT (g)	Ca	Mg	K	P	Mn	Fe	Cu	Zn	Al
		----------	----------	%	----------	----------	----------	mg/kg	----------	----------
					ULTISOL *					
Control-BF	0.28 d	0.37 c	0.29 d	1.64 c	0.27 c	68 cb	164 b	11 b	44 c	45 a
Control+BF	0.30 d	0.44 b	0.30 dc	2.70 b	0.37 ba	52 d	233 ba	18 a	69 bc	45 a
Sludge, 5 g/kg	0.36 cd	0.47 b	0.33 c	2.61 b	0.38 a	53 cd	368 ba	14 ba	83 b	48 a
Sludge, 10 g/kg	0.55 b	0.48 b	0.36 b	2.76 b	0.28 c	73 b	427 a	12 b	131 ba	38 a
Cowpea, 5 g/kg	0.49 cb	0.48 b	0.39 ba	3.47 a	0.30 bc	105 a	172 b	12 b	86 b	36 a
Cowpea, 10 g/kg	1.18 a	0.54 a	0.41 a	3.41 a	0.18 d	110 a	210 b	6.7 c	97 ba	34 a
Pr>F	0.0001	0.0002	0.0001	0.0001	0.0005	0.0001	0.0955	0.0019	0.0044	0.1960
					OXISOL					
Control-BF	0.46 c	0.81 a	0.62 a	2.55 c	0.21 bdc	2383 a	28 c	9.7 b	89.3 c	31 b
Control+BF	0.82 a	0.71 a	0.66 a	3.26 b	0.19 dc	1283 d	37 bc	10 b	117 ba	31 b
Sludge, 5 g/kg	0.77 a	0.73 a	0.70 a	3.02 b	0.16 d	1531 dc	56 a	12 ba	115 ba	27 b
Sludge, 10 g/kg	0.63 b	0.81 a	0.76 a	3.21 b	0.26 bac	1693 c	47 ba	13 a	130 a	40 a
Cowpea, 5 g/kg	0.74 a	0.81 a	0.69 a	3.50 a	0.26 ba	1578 c	50 a	12 ba	109 b	32 b
Cowpea, 10 g/kg	0.59 b	0.95 b	0.73 a	3.75 a	0.29 a	1886 b	48 ba	14 a	103 bc	29 b
Pr>F	0.0001	0.0848	0.482	0.0001	0.0136	0.0001	0.0117	0.0146	0.0049	0.0395
					MIXED SOIL					
Control-BF	0.54 c	0.55 a	0.48 a	2.50 b	0.19 b	1300 ba	34 c	11 a	85.3 d	37 a
Control+BF	0.72 a	0.59 a	0.56 a	3.10 a	0.25 a	1050 c	69 b	12 a	111 c	35 a
Sludge, 5 g/kg	0.64 b	0.58 a	0.56 a	2.87 a	0.26 a	1117 bc	78 ba	12 a	142 b	28 a
Sludge, 10 g/kg	0.61 cb	0.58 a	0.44 a	2.87 a	0.28 a	1225 bac	90 a	13 a	161 a	29 a
Cowpea, 5 g/kg	0.74 a	0.58 a	0.53 a	3.00 a	0.26 a	1300 ba	72 b	11 a	106 c	36 a
Cowpea, 10 g/kg	0.65 b	0.59 a	0.51 a	2.87 a	0.27 a	1397 a	73 b	12 a	115 c	24 a
Pr>F	0.0004	0.9038	0.2668	0.0337	0.003	0.0193	0.0001	0.3315	0.0001	0.2335

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.5 Soil solution composition and KCl-extractable Al in the Ultisol, Oxisol, and the mixed soil as affected by basal fertilizer, green manure, and sewage sludge application at low pH (4.0-5.0)

TREATMENTS	pH	EC dS/m	C	Total Al	Monomeric Al	Mn	Ca	Mg	K	Na	KCl-ext. Al cmol/kg
						mg/L					
					ULTISOL *						
Control-BF	3.61 f	1.72 e	64 d	44.8 a	42.5 a	1.00 d	31 e	44 e	13 d	62 d	2.80 a
Control+BF	4.06 e	3.65 d	63 d	2.92 b	2.82 b	1.53 c	91 d	56 d	509 c	61 d	2.10 b
Sludge, 5 g/kg	4.27 d	4.48 c	93 c	1.05 c	0.97 c	1.70 cb	113 c	64 c	491 c	116 b	1.60 c
Sludge, 10 g/kg	4.38 b	5.31 a	117 a	0.78 dc	0.69 c	1.97 b	147 b	82 b	519 c	164 a	1.37 e
Cowpea, 5 g/kg	4.33 c	4.53 c	90 c	0.87 dc	0.79 c	1.90 b	140 b	65 c	612 b	67 d	1.47 d
Cowpea, 10 g/kg	4.46 a	4.75 b	109 b	0.50 d	0.43 c	2.63 a	174 a	91 a	683 a	78 c	1.08 f
Pr>F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
					OXISOL						
Control-BF	4.55 e	3.55 d	41.7 e	0.37 a	0.35 a	154 a	236 b	143 e	126 d	63 d	1.12 a
Control+BF	4.93 d	4.39 c	52.3 d	0.16 b	0.13 b	83 d	186 e	157 d	274 c	70 c	0.52 b
Sludge, 5 g/kg	5.17 c	4.91 b	66.7 c	0.08 c	0.07 c	86 d	202 d	171 c	276 c	117 b	0.29 c
Sludge, 10 g/kg	5.22 c	5.50 a	85.0 a	0.05 d	0.03 d	97 c	215 c	184 b	282 c	154 a	0.24 c
Cowpea, 5 g/kg	5.33 b	4.48 c	67.0 c	0.04 ed	0.02 d	94 c	245 b	177 c	333 b	62 d	0.23 c
Cowpea, 10 g/kg	5.54 a	5.00 b	80.7 b	0.01 e	0.01 d	107 b	267 a	197 a	399 c	68 dc	0.10 d
Pr>F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
					MIXED SOIL						
Control-BF	4.28 d	2.50 f	50.7 d	1.39 a	1.34 a	72 a	123 c	88 d	71 d	52 d	1.67 a
Control+BF	4.58 c	3.97 e	70.3 c	0.27 b	0.25 b	43 d	102 d	105 c	324 c	67 c	0.95 b
Sludge, 5 g/kg	4.75 b	4.67 c	86.7 b	0.14 c	0.12 c	44 d	112 dc	112 c	329 c	116 b	0.63 c
Sludge, 10 g/kg	4.86 a	5.31 a	99.3 a	0.09 d	0.07 d	49 c	163 b	132 b	335 c	152 a	0.38 e
Cowpea, 5 g/kg	4.77 b	4.45 d	76.3 c	0.10 d	0.09 dc	46 dc	164 b	128 b	410 b	68 c	0.56 d
Cowpea, 10 g/kg	4.92 a	4.87 b	91.3 b	0.07 d	0.06 d	58 b	206 a	150 a	508 a	72 c	0.28 f
Pr>F	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.6 DTPA-extractable Fe, Mn, Cu, and Zn in the Ultisol, Oxisol, and the mixed soil as affected by sewage sludge and green manure application at low pH.*

TREATMENTS	Fe	Mn	Cu	Zn
	mg kg^{-1}			
		ULTISOL		
Control-BF	273 c	6.40 d	2.5 d	1.0 d
Control+BF	340 b	11.3 b	6.4 b	5.2 c
Sludge, 5 g kg^{-1}	339 b	10.2 c	6.5 b	9.2 b
Sludge, 10 g kg^{-1}	370 a	9.90 c	7.4 a	13.4 a
Cowpea, 5 g kg^{-1}	334 b	11.8 b	5.6 c	5.8 c
Cowpea, 10 g kg^{-1}	341 b	14.1 a	5.6 c	5.3 c
Pr>F	0.0001	0.0001	0.0001	0.0001
		OXISOL		
Control-BF	29.3 d	316 a	5.53 c	5.27 d
Control+BF	32.3 dc	264 c	7.27 b	9.01 c
Sludge, 5 g kg^{-1}	39.3 b	284 bc	8.11 a	13.1 b
Sludge, 10 g kg^{-1}	45.3 a	280 bc	8.52 a	15.0 a
Cowpea, 5 g kg^{-1}	33.0 dc	277 bc	6.89 b	8.90 c
Cowpea, 10 g kg^{-1}	35.0 c	297 ba	7.21 b	9.71 c
Pr>F	0.0001	0.0089	0.0001	0.0001
		MIXED SOIL		
Control-BF	138 b	177 bc	4.31 c	3.30 d
Control+BF	140 b	167 c	6.48 b	6.80 c
Sludge, 5 g kg^{-1}	142 b	165 c	6.94 b	10.9 b
Sludge, 10 g kg^{-1}	154 a	170 c	7.97 a	14.1 a
Cowpea, 5 g kg^{-1}	140 b	193 ba	6.76 b	7.70 c
Cowpea, 10 g kg^{-1}	142 b	211 a	6.42 b	7.20 c
Pr>F	0.0006	0.0019	0.0001	0.0001

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.7 Shoot growth and composition of soybeans as affected by green manure addition to the Ultisol, Oxisol, and the mixed soil at neutral pH.

TREATMENTS	DRY WEIGHT g	Ca	Mg	K	P	Mn	Fe	Cu	Zn
		%				mg/kg			
				ULTISOL *					
Control	1.65 b	0.65 a	0.31 a	2.74 a	0.13 a	71 a	110 a	12.7 a	31.7 b
Cowpea, 5 g/kg	1.74 ba	0.65 a	0.32 a	2.70 a	0.14 a	76 a	113 b	12.0 a	35.0 ba
Cowpea, 10 g/kg	1.78 a	0.62 a	0.33 a	2.88 a	0.15 a	77 a	180 b	13.7 a	38.0 a
P>F	0.0723	0.8277	0.5559	0.6076	0.8178	0.3803	0.0120	0.7127	0.0327
				OXISOL					
Control	1.71 a	0.85 a	0.45 a	2.02 b	0.11 a	176 c	99.7 a	14 a	54 b
Cowpea, 5 g/kg	1.43 b	0.71 b	0.44 a	2.36 ba	0.12 a	202 b	85.3 ba	13 a	71 ba
Cowpea, 10 g/kg	1.29 b	0.69 b	0.43 a	2.71 a	0.13 a	234 c	67.0 b	15 a	77 a
P>F	0.0047	0.0067	0.9698	0.0938	0.1729	0.0004	0.0435	0.7703	0.0644
				MIXED SOIL					
Control	1.60 a	0.80 a	0.43 a	2.31 b	0.11 a	116 b	107 a	11.0 b	44 b
Cowpea, 5 g/kg	1.61 a	0.73 a	0.42 a	2.67 a	0.12 a	130 b	112 a	12.3 ba	53 a
Cowpea, 10 g/kg	1.67 a	0.82 a	0.45 a	2.70 a	0.13 a	173 a	132 a	15.3 a	60 a
P>F	0.5958	0.6734	0.8371	0.0069	0.2160	0.0060	0.8451	0.0859	0.0053

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.8 Soil solution composition and extractable P in the Ultisol, Oxisol, and the mixed soil as affected by green manure application at neutral pH

	pH	EC	C	Ca	Mg	K	Na	Mn	Extrac. P
TREATMENTS		dS/m				mg/L			mg/kg
				ULTISOL *					
Control	6.07 c	1.79 b	72 c	167 c	12.9 c	245 c	32 c	0.37 a	21.3 a
Cowpea, 5 g/kg	6.32 b	2.54 a	88 b	200 b	19.1 b	330 b	38 b	0.47 a	22.3 a
Cowpea, 10 g/kg	6.57 a	2.93 a	108 a	247 a	25.0 a	402 a	43 a	0.50 a	20.7 a
P>F	0.0009	0.0117	0.0002	0.0010	0.0001	0.0001	0.0003	0.0746	0.7039
				OXISOL					
Control	6.27 c	2.33 c	63 c	536 c	65.1 c	177 c	56 a	2.33 c	45.7 b
Cowpea, 5 g/kg	6.59 b	3.10 b	85 b	595 b	84.2 b	209 b	55 a	6.73 b	50.3 a
Cowpea, 10 g/kg	6.83 a	3.43 a	101 c	617 c	98.8 a	240 c	63 a	12.80 a	51.7 a
P>F	0.0001	0.0001	0.0001	0.0003	0.0001	0.0001	0.2296	0.0001	0.0159
				MIXED SOIL					
Control	6.12 c	2.33 c	69 c	351 b	42 c	231 c	48 a	1.43 c	35.7 a
Cowpea, 5 g/kg	6.38 a	2.68 b	92 b	408 a	57 b	274 b	55 a	2.90 b	36.3 a
Cowpea, 10 g/kg	6.54 c	3.01 a	106 a	447 a	76 a	320 c	57 a	4.30 a	37.7 a
P>F	0.0001	0.0003	0.0001	0.0034	0.0001	0.0001	0.1873	0.0010	0.5008

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.9 DTPA-extractable Fe, Mn, Cu, and Zn in the Ultisol, Oxisol, and the mixed soil as affected by green manure application at medium pH.*

TREATMENTS	Fe	Mn	Cu	Zn
	mg kg^{-1}			
		ULTISOL		
Control+BF	52 a	5.87 c	3.64 a	3.13 a
Cowpea, 5 g kg^{-1}	43 b	7.50 b	3.97 a	3.23 a
Cowpea, 10 g kg^{-1}	41 b	10.8 a	8.83 a	3.36 a
Pr>F	0.0163	0.0003	0.3909	0.3857
		OXISOL		
Control+BF	15.7 a	139 b	6.20 a	5.70 a
Cowpea, 5 g kg^{-1}	15.3 a	205 a	5.80 a	5.73 a
Cowpea, 10 g kg^{-1}	16.6 a	225 a	5.90 a	6.70 a
Pr>F	0.3075	0.0002	0.3516	0.3558
		MIXED SOIL		
Control+BF	25.3 b	95 c	4.74 a	4.90 a
Cowpea, 5 g kg^{-1}	26.3 b	110 b	5.37 a	5.20 a
Cowpea, 10 g kg^{-1}	29.0 a	129 a	5.80 a	6.30 a
Pr>F	0.0024	0.0012	0.3876	0.1269

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.10. Concentrations of Ca, Mg, and K released (mg kg^{-1}) into the soil solution of the Ultisol, Oxisol, and the mixed soil from cowpea green manure application at neutral pH.

Soil	Cowpea manure g kg^{-1}	Ca	Mg	K
		mg L^{-1}		
Ultisol	5	33	6.2	85
	10	80	12.1	157
Oxisol	5	59	19.1	32
	10	81	33.7	63
Mixed soil	5	57	15.0	43
	10	96	34.0	89

Table 4.11 Shoot growth and composition of soybeans as affected by green manure addition to the Ultisol, Oxisol and the mixed soil at alkaline pH.

TREATMENTS	DRY WEIGHT g/pot	Ca	Mg	K	P	Mn	Fe	Cu	Zn
		%				mg/kg			
					ULTISOL *				
Control	0.57 c	0.78 a	0.24 a	2.34 b	0.19 a	34 a	49.7 c	8.33 a	18.7 a
Cowpea, 5 g/kg	0.72 b	0.89 a	0.23 a	2.30 a	0.19 a	35 a	64.7 b	9.50 a	23.3 a
Cowpea, 10 g/kg	1.11 a	0.89 a	0.27 a	2.78 a	0.19 a	46 a	82.7 a	10.70 a	22.3 a
P>F	0.0002	0.1938	0.6662	0.0392	0.9832	0.2320	0.0003	0.1630	0.4767
					OXISOL				
Control	0.70 b	1.14 a	0.34 a	3.17 a	0.15 a	38.3 a	52.0 b	10.3 a	25.0 a
Cowpea, 5 g/kg	0.73 ba	1.04 ba	0.33 a	3.29 a	0.17 a	39.0 a	57.0 b	12.0 a	24.0 ba
Cowpea, 10 g/kg	0.88 a	0.97 b	0.31 a	3.56 a	0.19 a	54.0 a	70.0 a	11.8 a	21.0 b
P>F	0.0960	0.0362	0.6894	0.2615	0.3374	0.0990	0.0093	0.6864	0.0704
					MIXED SOIL				
Control	0.83 a	0.99 a	0.30 a	3.28 ba	0.14 a	36.3 b	61.3 a	8.50 b	20.2 a
Cowpea, 5 g/kg	0.93 a	0.99 a	0.32 a	3.16 b	0.15 a	38.7 ba	73.3 a	9.33 ba	23.0 a
Cowpea, 10 g/kg	1.00 a	0.88 a	0.33 a	3.62 a	0.16 a	46.0 a	77.7 a	10.40 a	23.7 a
P>F	0.2556	0.0017	0.5182	0.0716	0.3099	0.0498	0.1156	0.0599	0.6433

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

Table 4.12 Soil solution composition and extractable P in the Ultisol, Oxisol, and the mixed soil as affected by green application at alkaline pH

	pH	EC	C	Ca	Mg	K	Na	Mn	Extrac. P
TREATMENTS		dS/m	----------	----------	mg/L	----------	----------		mg/kg
				ULTISOL *					
Control	7.56 b	2.68 c	133 b	402 c	5.03 c	252 c	31 b	0.17 a	26.3 b
Cowpea, 5 g/kg	7.73 a	2.97 b	153 b	450 b	8.10 b	329 b	38 a	0.30 a	30.0 ba
Cowpea, 10 g/kg	7.82 a	3.34 a	207 a	487 c	10.90 c	393 a	39 a	0.40 a	34.3 a
P>F	0.0023	0.0001	0.0037	0.0001	0.0001	0.0001	0.0001	0.2230	0.0421
				OXISOL					
Control	7.55 c	3.36 c	105 c	882 b	22 c	154 b	39.7 c	0.50 a	61.0 b
Cowpea, 5 g/kg	7.75 b	3.97 b	127 b	966 a	34 b	188 ba	44.3 b	0.33 b	63.7 ba
Cowpea, 10 g/kg	7.87 a	4.47 a	150 a	967 a	54 a	226 a	50.8 a	0.60 a	65.3 a
P>F	0.0001	0.0001	0.0001	0.0072	0.0001	0.0108	0.0001	0.0076	0.0320
				MIXED SOIL					
Control	7.48 c	2.93 c	123 c	718 b	13.5 c	209 c	32.8 b	0.40 a	38 b
Cowpea, 5 g/kg	7.67 b	3.67 b	164 b	740 ba	20.2 b	255 b	35.8 ba	0.53 a	40 b
Cowpea, 10 g/kg	7.82 a	4.04 a	190 a	760 a	25.7 a	284 a	39.3 a	0.37 a	46 a
P>F	0.0039	0.0001	0.0001	0.0294	0.0001	0.0001	0.0353	0.4506	0.0369

* Means not followed by the same letter are significantly different according to the LSD test.

Table 4.13 DTPA-extractable Fe, Mn, Cu, and Zn in the Ultisol, Oxisol, and the mixed soil as affected by green manure application at alkaline.*

TREATMENTS	Fe	Mn	Cu	Zn
	mg kg^{-1}			
		ULTISOL		
Control+BF	32 a	3.27 c	2.97 a	2.83 a
Cowpea, 5 g kg^{-1}	33 a	4.07 b	2.85 a	2.90 a
Cowpea, 10 g kg^{-1}	34 a	5.20 a	3.01 a	3.30 a
Pr>F	0.5120	0.0001	0.6878	0.3808
		OXISOL		
Control+BF	10.7 b	87 ba	4.9 b	5.90 a
Cowpea, 5 g kg^{-1}	11.0 b	83 ba	5.2 ba	5.84 a
Cowpea, 10 g kg^{-1}	12.3 a	100 a	5.3 a	6.63 a
Pr>F	0.0110	0.0531	0.1098	0.1426
		MIXED SOIL		
Control+BF	20.0 a	39.5 c	4.01 b	4.07 b
Cowpea, 5 g kg^{-1}	20.7 a	54.1 b	4.42 a	4.97 ba
Cowpea, 10 g kg^{-1}	21.3 a	66.0 a	4.39 ba	5.57 a
Pr>F	0.2963	0.0035	0.0722	0.0375

* Means not followed by the same letter are significantly different at $P < 0.05$ according to the LSD test.

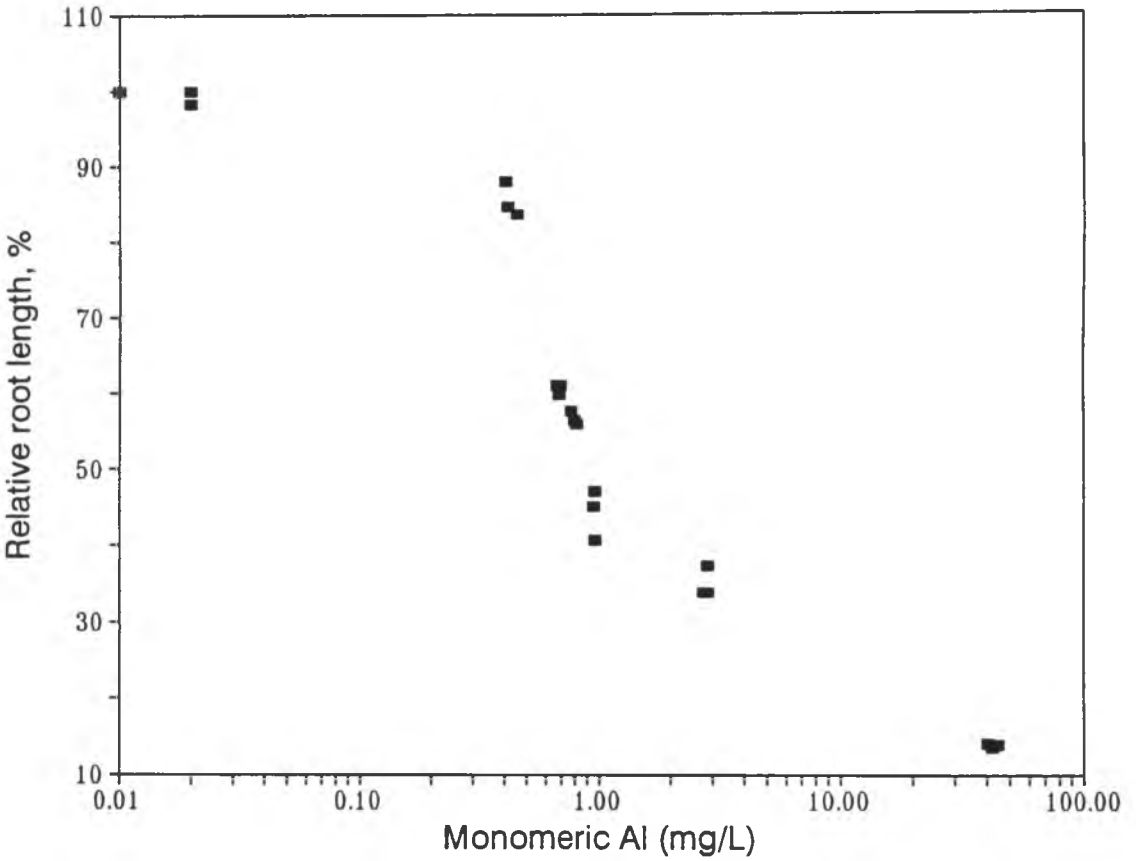

Fig 4.1 Relationship between monomeric Al and relative root length of Forrest soybean grown in the Paaloa Ultisol

Appendix A. Analysis of Variance for effects of soil types, treatments, and their interactions on root growth and composition at low pH.

	Probability > F			
Source	Root Biomass	Root Al	Root Length	Root Mn
Soil	0.0057	0.0001	0.0001	0.0001
Treatments	0.0001	0.0001	0.0001	0.0001
Soil*Trts	0.0001	0.0001	0.0001	0.0002

Appendix B. Analysis of variance for effect of soil types, treatments, and their interactions on shoot growth and composition at low pH.

Probability > F

	Source		
Variables	Soil	Treat.	Soil*Treat
Dry matter	0.0001	0.0001	0.0001
Ca	0.0001	0.0025	0.0735
Mg	0.0001	0.1287	0.1878
K	0.0001	0.0001	0.0001
P	0.0001	0.0275	0.0001
Mn	0.0001	0.0001	0.0001
Fe	0.0001	0.0137	0.0521
Cu	0.5196	0.0043	0.0001
Zn	0.0001	0.0001	0.0382
Al	0.0001	0.0934	0.0793

Appendix C. Analysis of variance for effect of soil types, treatments, and their interactions on soil composition at low pH.

	Probability > F		
	Source		
Variables	Soil	Treat.	Soil*Treat
Soluble pH	0.0001	0.0001	0.0001
Soluble EC	0.0001	0.0001	0.0001
Soluble C	0.0001	0.0001	0.0001
Soluble monomeric Al	0.0001	0.0001	0.0001
Soluble total Al	0.0001	0.0001	0.0001
Soluble Mn	0.0001	0.0001	0.0001
Soluble Ca	0.0001	0.0001	0.0001
Soluble Mg	0.0001	0.0001	0.0328
Soluble K	0.0001	0.0001	0.0001
Soluble Na	0.1649	0.0001	0.0273
DTPA-extractable Fe	0.0001	0.0001	0.0001
DTPA-extractable Mn	0.0001	0.0001	0.0001
DTPA-extractable Zn	0.0001	0.0001	0.0656
DTPA-extractable Cu	0.0001	0.0001	0.0001
KCl-extr. Al	0.0001	0.0001	0.0001

Appendix D. Analysis of variance for effect of soil types, treatments, and their interactions on shoot growth and composition at neutral pH.

	Probability > F		
	Source		
Variables	Soil	Treat.	Soil*Treat
Dry matter	0.0001	0.1532	0.0001
Ca	0.0068	0.1878	0.4279
Mg	0.0003	0.7837	0.9441
K	0.0054	0.0058	0.2711
P	0.0861	0.2754	0.9892
Mn	0.0001	0.0001	0.0008
Fe	0.0207	0.6911	0.1046
Cu	0.5628	0.1594	0.7941
Zn	0.0001	0.0002	0.2286

Appendix E. Analysis of variance for effect of soil types, treatments, and their interactions on shoot growth and composition at alkaline pH.

	Probability > F		
	Source		
Variables	Soil	Treat.	Soil*Treat
Dry matter	0.0062	0.0001	0.0101
Ca	0.0001	0.0844	0.0043
Mg	0.0057	0.7054	0.7298
K	0.0001	0.0038	0.4118
P	0.0162	0.1919	0.7549
Mn	0.3151	0.0029	0.9149
Fe	0.0046	0.0001	0.1210
Cu	0.0369	0.0784	0.9573
Zn	0.3807	0.4527	0.4286

Appendix F. Analysis of variance for effect of soil types, treatments, and their interactions on soil composition at neutral pH.

	Probability > F		
	Source		
Variables	Soil	Treat.	Soil*Treat
Soil solution			
pH	0.0001	0.0001	0.3179
EC	0.0001	0.0001	0.2101
C	0.0006	0.0001	0.2977
Mn	0.0001	0.0001	0.0001
Ca	0.0001	0.0001	0.4934
Mg	0.0001	0.0001	0.0001
K	0.0001	0.0001	0.0001
Na	0.0001	0.0016	0.5791
DTPA-extractable			
Fe	0.0001	0.0299	0.0001
Mn	0.0001	0.0001	0.0001
Zn	0.0001	0.0290	0.6091
Cu	0.8662	0.2849	0.4420
$NaHCO_3$-extractable P	0.0001	0.0467	0.1083

Appendix G. Analysis of variance for effect of soil types, treatments, and their interactions on soil composition at alkaline pH.

	Probability > F		
	Source		
Variables	Soil	Treat.	Soil*Treat
Soil solution			
pH	0.0486	0.0001	0.7538
EC	0.0001	0.0001	0.0001
C	0.0001	0.0001	0.0419
Mn	0.0170	0.2795	0.0570
Ca	0.0001	0.0001	0.0259
Mg	0.0001	0.0001	0.0001
K	0.0001	0.0001	0.0001
Na	0.0001	0.0001	0.0367
DTPA-extractable			
Fe	0.0001	0.0445	0.9818
Mn	0.0001	0.0001	0.0030
Zn	0.0001	0.0203	0.0401
Cu	0.0001	0.0279	0.2464
NaHC03-extractable P	0.0001	0.0001	0.5892

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